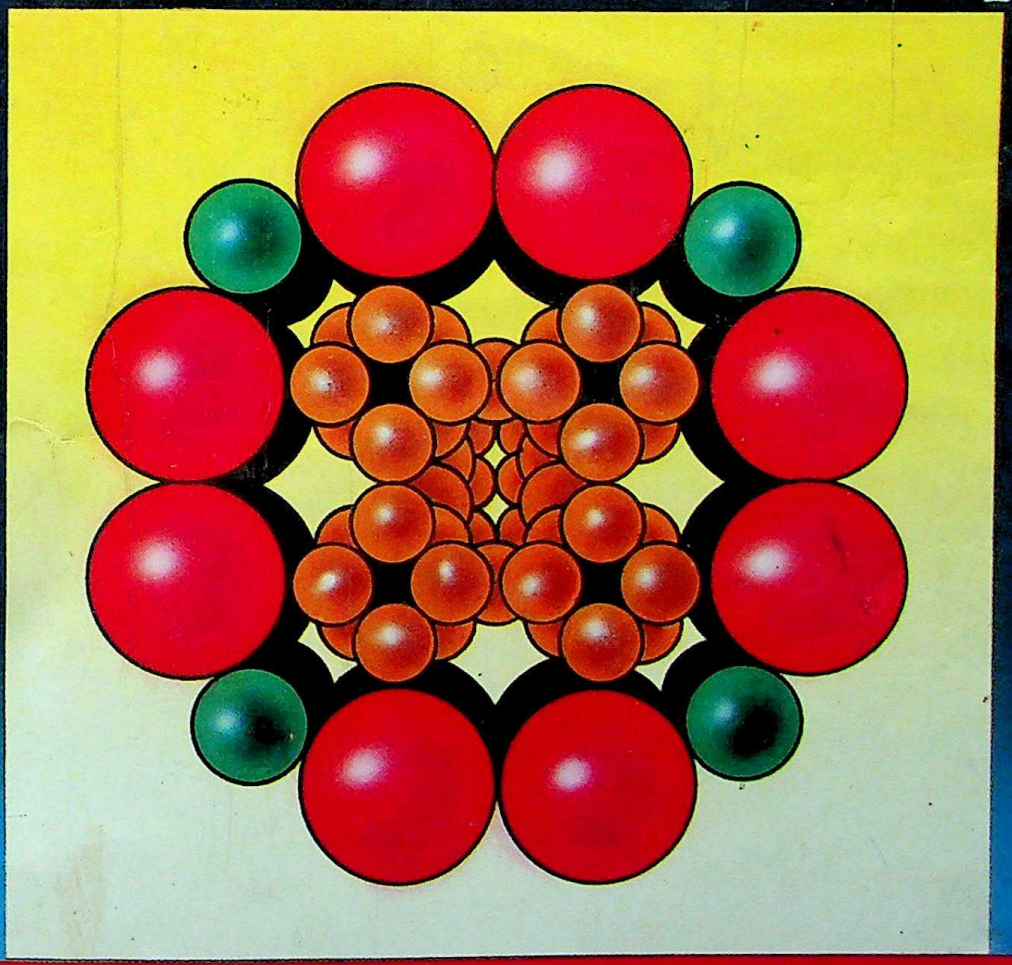
Comprehensive Chemistry



CLASS XII

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JOB\T1

Representative Elements

|⟵ *s*-block ⟶|

GROUPS

LONG FORM OF PERIODI

Transition Elements

⟵ *d*-block ⟶

PERIODS	1	2	3	4	5	6	7	8
1	1 H $1s^1$							
2	3 Li $2s^1$	4 Be $2s^2$						
3	11 Na $3s^1$	12 Mg $3s^2$						
4	19 K $4s^1$	20 Ca $4s^2$	21 Sc $3d^14s^2$	22 Ti $3d^24s^2$	23 V $3d^34s^2$	24 Cr $3d^54s^1$	25 Mn $3d^54s^2$	26 Fe $3d^64s^2$
5	37 Rb $5s^1$	38 Sr $5s^2$	39 Y $4d^15s^2$	40 Zr $4d^25s^2$	41 Nb $4d^45s^1$	42 Mo $4d^55s^1$	43 Tc $4d^55s^2$	44 Ru $4d^75s^1$
6	55 Cs $6s^1$	56 Ba $6s^2$	57 La* $5d^16s^2$	72 Hf $4f^{14}5d^26s^2$	73 Ta $5d^36s^2$	74 W $5d^46s^2$	75 Re $5d^56s^2$	76 Os $5d^66s^2$
7	87 Fr $7s^1$	88 Ra $7s^2$	89 Ac** $6d^17s^2$	104 Ku	105 Ha	106 Unh	107 Uns	

Inner Transition El

⟵ *f*-block ⟶

*Lanthanides $4f^n5d^{0-1}6s^2$	58 Ce $4f^15d^16s^2$	59 Pr $4f^35d^06s^2$	60 Nd $4f^45d^06s^2$	61 Pm $4f^55d^06s^2$	62 Sm $4f^65d^06s^2$	63 Eu $4f^75d^06s^2$	64 Gd $4f^75d^16s^2$	65 Tb $4f^95d^0$
**Actinides $5f^n6d^{0-1}7s^2$	90 Th $5f^06d^27s^2$	91 Pa $5f^26d^17s^2$	92 U $5f^36d^17s^2$	93 Np $5f^46d^17s^2$	94 Pu $5f^66d^07s^2$	95 Am $5f^76d^07s^2$	96 Cm $5f^76d^17s^2$	97 Bk $5f^96d^0$

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Representative Elements

p-block

Noble gases

DIC TABLE

13	14	15	16	17	18
					2 He $1s^2$
5 B $2s^2 2p^1$	6 C $2s^2 2p^2$	7 N $2s^2 2p^3$	8 O $2s^2 2p^4$	9 F $2s^2 2p^5$	10 Ne $2s^2 2p^6$
13 Al $3s^2 3p^1$	14 Si $3s^2 3p^2$	15 P $3s^2 3p^3$	16 S $3s^2 3p^4$	17 Cl $3s^2 3p^5$	18 Ar $3s^2 3p^6$
31 Ga $4s^2 4p^1$	32 Ge $4s^2 4p^2$	33 As $4s^2 4p^3$	34 Se $4s^2 4p^4$	35 Br $4s^2 4p^5$	36 Kr $4s^2 4p^6$
49 In $5s^2 5p^1$	50 Sn $5s^2 5p^2$	51 Sb $5s^2 5p^3$	52 Te $5s^2 5p^4$	53 I $5s^2 5p^5$	54 Xe $5s^2 5p^6$
81 Tl $6s^2 6p^1$	82 Pb $6s^2 6p^2$	83 Bi $6s^2 6p^3$	84 Po $6s^2 6p^4$	85 At $6s^2 6p^5$	86 Rn $6s^2 6p^6$

s

9	10	11	12
27 Co $3d^7 4s^2$	28 Ni $3d^8 4s^2$	29 Cu $3d^{10} 4s^1$	30 Zn $3d^{10} 4s^2$
45 Rh $4d^8 5s^1$	46 Pd $4d^{10}$	47 Ag $4d^{10} 5s^1$	48 Cd $4d^{10} 5s^2$
77 Ir $5d^7 6s^2$	78 Pt $5d^9 6s^1$	79 Au $5d^{10} 6s^1$	80 Hg $5d^{10} 6s^2$

lements

5 b $d^0 6s^2$	66 Dy $4f^{10} 5d^0 6s^2$	67 Ho $4f^{11} 5d^0 6s^2$	68 Er $4f^{12} 5d^0 6s^2$	69 Tm $4f^{13} 5d^0 6s^2$	70 Yb $4f^{14} 5d^0 6s^2$	71 Lu $4f^{14} 5d^1 6s^2$
7 k $d^0 7s^2$	98 Cf $5f^{10} 6d^0 7s^2$	99 Es $5f^{11} 6d^0 7s^2$	100 Fm $5f^{12} 6d^0 7s^2$	101 Md $5f^{13} 6d^0 7s^2$	102 No $5f^{14} 6d^0 7s^2$	103 Lr $5f^{14} 6d^1 7s^2$

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PREFACE—Eighth Edition

We have immense pleasure to bring out the Eighth Revised Edition of Comprehensive Chemistry for Class XII students. The book not only aims at preparing the students for various board examinations but also attempts to provide upto date knowledge for the Competitive/Entrance Examinations of various engineering and medical colleges. The text has been revised in the light of the suggestions received from respected teachers and the students from all over the country. The significant features of this edition are :

★ *The subject matter is in full conformity with the syllabi prescribed by the CBSE New Delhi and education boards of other Indian states.*

★ *The text has been made simple and upto date to keep pace with the changing trends of education at the national level.*

★ *A brief recap along with important formulae is given just before the exercise in each unit.*

★ *Competition file containing MCQ, True false statements, Fill in the blanks, etc., are given in each unit under the heading FOR THE COMPETITIVE EXAMINATIONS.*

★ *The organic chemistry section has been thoroughly revised and elaborated so as to meet the requirements of board examinations and also that of various competitive examinations.*

★ *Nomenclature of organic compounds and certain basic concepts of organic chemistry have been given in Chapter 7A.*

★ *Name reactions and important routes to organic conversions are separately discussed is chapter 9-A.*

★ *Mechanism of important organic reactions, and some additional concepts are given in boxes in different chapters in order to provide better understanding.*

★ *In each chapter a large number of short-answer questions have been given in the form of review problems.*

★ *A large number of numericals (solved as well as unsolved) have been added wherever required.*

★ *Answer to the numericals have been carefully checked to minimise the errors.*

★ *Hints to the typical questions are given at the end of each chapter.*

★ *Important questions appeared in the recent examinations have been included in the respective chapters.*

We express our sincere thanks to **M/s Laxmi Publications** and their staff for bringing out the present edition of this book. We also express our sense of gratefulness to dear students and worthy teachers who have been kind enough to draw our attention to errors and omissions in previous editions.

We sincerely hope that the book in the present revised form will be well received by the students as well as by our learned colleagues. Further suggestions for the improvement of the book are welcomed and will be gratefully acknowledged.

—AUTHORS

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PREFACE TO THE FIRST EDITION

With immense pleasure we present this book for the students of class XII under the 10 + 2 pattern of education. The book has been written strictly according to the new syllabus issued by Central Board of Secondary Education for their examinations to be held in 1991 onwards. While developing the text special attempt has been made to keep the language and presentation as simple, concise and free of confusion as possible.

Some salient features of the book are :

- ★ The text is strictly based upon the guidelines and the syllabus issued by C.B.S.E.
- ★ The text has been written in lucid and elegant style.
- ★ All definitions and important statements have been given in italics.
- ★ Wherever required a large number of solved as well as unsolved numerical problems are included.
- ★ For self-evaluation a large number of objective as well as subjective questions have been included at the end of each units.
- ★ A large number of organic conversions and fill in the blanks, alongwith their answers, have been given in appendices I and II.
- ★ Throughout the text S.I. Units have been adopted.

We earnestly hope that the book will be appreciated by our learned colleagues and students. Constructive suggestions for the improvement of the text shall be gladly acknowledged.

—AUTHORS

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SYLLABUS

CHEMISTRY—CLASS XII (Theory)

One Paper (Theory) **3 hours** **70 marks**

Unitwise Weightage

Unit		*Marks*
1.	Atomic Structure and Chemical Bonding	4
2.	The Solid State	3
3.	Solutions	5
4.	Chemical Thermodynamics	5
5.	Electrochemistry	4
6.	Chemical Kinetics	4
7.	Organic Chemistry Based on Functional Groups—I Halides and Hydroxy Compounds	5
8.	Organic Chemistry Based on Functional Groups—II	5
9.	Organic Chemistry Based on Functional Groups—III	5
10.	Chemistry of Representative Elements	6
11.	Transition Metals Including Lanthanides	6
12.	Co-ordination Chemistry and Organometallics	3
13.	Nuclear Chemistry	3
14.	Synthetic and Natural Polymers	2
15.	Surface Chemistry	3
16.	Bio-Molecules	3
17.	Chemistry of Biological Processes	2
18.	Chemistry in Action	2

Unit 1 : Atomic Structure and Chemical Bonding — 10 Pds.

Atoms : dual nature of matter and radiation. The de-Broglie relation. Uncertainty principle. Orbitals and quantum numbers. Shapes of orbitals. Electronic configuration of atoms. Molecules : Molecular orbital method. Hybridisation—involving *s*, *p*, *d* orbitals.

Unit 2 : The Solid State — 7 Pds.

Structure of simple ionic compounds. Close-packed structures. Ionic-radii, Silicates (elementary ideas). Imperfection in solids (Point defects only). Properties of solids, amorphous solids.

Unit 3 : Solutions — 12 Pds.

Types of solutions. Vapour-pressure of solutions and Raoult's law. Colligative properties. Non-ideal solutions and abnormal molecular masses.

Unit 4 : Chemical Thermodynamics — 12 Pds.

First law of thermodynamics : Internal energy, enthalpy, application of first law of thermodynamics.

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Second law of thermodynamics : Entropy, free energy, spontaneity of a chemical reaction, free energy change and chemical equilibrium, free energy as energy available for useful work.

Third law of thermodynamics.

Unit 5 : Electrochemistry 10 Pds.

Electrolytic conduction. Voltaic cell. Electrode potential and electromotive force. Gibb's free energy and cell potential. Electrode potential and electrolysis. Primary cells including fuel cells. Corrosion.

Unit 6 : Chemical Kinetics 10 Pds.

Rate expression. Order of a reaction (with suitable examples). Units of rates and specific rate constants. Order of reaction and effect of concentration (study will be confined to first order only). Temperature dependence of rate constant, fast reactions (only elementary idea). Photochemical reactions. Mechanism of reaction (only elementary idea).

Unit 7 : Organic Chemistry Based on Functional Groups I 12 Pds.

(*Halides and hydroxy compounds*)

Nomenclature of compounds containing halogen atoms and hydroxyl groups : Preparation, properties and uses of haloalkanes, haloarenes, alcohols and phenols. Correlation of physical properties.

Preparation, properties and uses of the following :

Polyhalogen compounds : chloroform, iodoform.

Polyhydric compounds : ethane-1, 2-diol ; Propane-1, 2, 3-triol.

Unit 8 : Organic Chemistry Based on Functional Groups II 12 Pds.

(*Ethers, aldehydes, ketones, carboxylic acids and their derivatives*)

Nomenclature of ethers, aldehydes, ketones, carboxylic acids and their derivatives. (acylhalides, acid anhydrides, amides and esters).

General methods of preparation, correlation of physical properties with their structures, chemical properties and uses.

[**Note** : Specific compounds should not be stressed for the purpose of evaluation.]

Unit 9 : Organic Chemistry Based on Functional Groups III 12 Pds.

(*Cyanides, isocyanides, nitro compounds and amines*)

Nomenclature of cyanides and isocyanides ; nitro compounds and amines ; and their methods of preparation ; correlation of physical properties with structure, chemical reactions and uses.

Unit 10 : Chemistry of Representative Elements 14 Pds.

The chemistry of *s*- and *p*-block elements, electronic configuration, general characteristic properties and oxidation states of the following :

Group 1 elements—Alkali metals.
Group 2 elements—Alkaline earth metals.
Group 13 elements—Boron family.
Group 14 elements—Carbon family.
Group 15 elements—Nitrogen family.
Group 16 elements—Oxygen family.
Group 17 elements—Halogen family.

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Group 18 elements—Noble gases.

Hydrogen.

Unit 11 : Transition Metals Including Lanthanides 14 Pds.

Electronic configuration : General characteristic properties, oxidation states of transition metals, atoms in their salts and compounds.

First row transition metals and general properties of their compounds—oxides, halides and sulphides.

General properties of second and third row transition elements (Groupwise discussion).

Preparation, properties and uses of potassium dichromate and potassium permanganate.

Inner transition elements : General discussion with special reference to oxidation states and Lanthanide contraction.

Unit 12 : Coordination Chemistry and Organometallics 7 Pds.

Co-ordination compounds : Nomenclature. Isomerism and Applications of coordination compounds. Compounds containing metal carbon bond ; Application of organometallics.

Unit 13 : Nuclear Chemistry 7 Pds.

Nature of radiation from radioactive substances.

Nuclear structure and nuclear properties, nuclear reactions ; radioactive disintegration series ; artificial transmutation of elements ; Nuclear fission and Nuclear fusion. Radio isotopes and their uses ; Carbon-dating ; Synthetic elements.

Unit 14 : Synthetic and Natural Polymers 5 Pds.

Classification of polymers, natural and synthetic polymers (with stress on their general methods of preparation) and important uses of the following : Teflon, PVC, Nylon-66, Terylene and synthetic rubber.

Unit 15 : Surface Chemistry 7 Pds.

Surfaces : Adsorption.

Colloids : Preparation and general properties.

Emulsions and micelles.

Catalysis : Homogeneous and heterogeneous, shape selective catalyst.

Unit 16 : Bio-Molecules 7 Pds.

Carbohydrates : monosaccharides, disaccharides, polysaccharides.

Amino acids. Peptides—structure and classification.

Proteins : structure and their role.

Nucleic acids—DNA and RNA.

Biological functions of nucleic acids—protein synthesis and replication.

Lipids—structure, membranes and their functions.

Unit 17 : Chemistry of Biological Processes 5 Pds.

Carbohydrates and their metabolism. Blood, haemoglobin and respiration ; Immune system ; Vitamins and hormones. Simple idea of chemical evolution.

Unit 18 : Chemistry in Action 5 Pds.

Dyes. Medicines, antipyretic, analgesic, antibiotics and tranquilisers. Rocket propellants.

(Structural formulae non-evaluative)

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MARKING SCHEME

1. C.B.S.E. & HARYANA BOARD

One Paper (Theory) **3 hours** **70 marks**

Unit No.	*Name of the Unit*	*Marks*
1.	Atomic Structure and Chemical Bonding	4
2.	The Solid State	3
3.	Solutions	5
4.	Chemical Thermodynamics	5
5.	Electrochemistry	4
6.	Chemical Kinetics	4
7.	Organic Chemistry Based on Functional Groups—I Halides and Hydroxy Compounds	5
8.	Organic Chemistry Based on Functional Groups—II	5
9.	Organic Chemistry Based on Functional Groups—III	5
10.	Chemistry of Representative Elements	6
11.	Transition Metals Including Lanthanides	6
12.	Coordination Chemistry and Organo Metallics	3
13.	Nuclear Chemistry	3
14.	Synthetic and Natural Polymers	2
15.	Surfaces Chemistry	3
16.	Bio-Molecules	3
17.	Chemistry of Biological Processes	2
18.	Chemistry in Action	2

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2. PANJAB SCHOOL EDUCATION BOARD

Structure of Question Paper

There will be six questions in all, one from each of the following groupings. Marks allotted to each question and its sub-unit have also been shown :

1.	(a)	Atomic Structure and Chemical Bonding	3
	(b)	Chemical Thermodynamics	5
	(c)	Co-ordination Chemistry and Organo Metallics	3
2.	(a)	The Solid State	3
	(b)	Solutions	5
	(c)	Nuclear and Radio Chemistry	3
3.	(a)	Electrochemistry	4
	(b)	Chemical Kinetics	4
	(c)	Surfaces and Catalysis	4
4.	(a)	Organic Chemistry Based on Functional Groups—I Halides and Hydroxy Compounds	5
	(b)	Organic Chemistry on Functional Groups—II	5
	(c)	Chemistry of Biological Processes	2
5.	(a)	Organic Chemistry on Functional Groups—III	5
	(b)	Synthetic and Natural Polymers	2
	(c)	Bio-molecules	3
	(d)	Chemistry in Action	2
6.	(a)	Chemistry of Representative Elements	6
	(b)	Transition Metals including Lanthanides	6

Notes

1. A candidate will have to attempt all the questions. However, there will be internal choice varying from 33—40% in all the questions.
2. There will be three types of questions. Approximate weightage given to each type will be as follows :
   (a) Descriptive type 20%
   (b) Short answer type 60%
   (c) Numerical problems 20%
3. There will not be any objective type question such as 'Yes' or 'No'/Tick (✔) or Cross (×), fill in the blanks/multiple choice, etc.
4. Question paper should be strictly from the prescribed syllabus and based on the above mentioned guidelines.

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1

Structure of Atoms and Molecules

LEARNING OBJECTIVES

In this Unit, we shall learn

Atoms :

- *the dual nature of matter and radiation ;*
- *The de-Broglie equation ;*
- *uncertainty principle ;*
- *orbitals and quantum numbers ;*
- *electronic configuration of elements ;*
- *shapes of orbitals ;*

Molecules :

- *molecular orbital method ;*
- *Hybridisation.*

The atomic concept of matter was put forward by Dalton (1808) to explain the laws of chemical combination. He considered the atoms as structureless indivisible particles. The inner structure of atoms was first of all proposed by Rutherford. He proposed that the atoms contain a positive centre, called *nucleus*, around which the electrons are revolving in circular paths. This model was, however, modified by Bohr who treated the electrons as particles and assigned to them *definite* circular paths called *orbits* around the nucleus. However, Bohr's idea of well-defined orbits came in direct conflict with modern principles such as dual nature of matter, which considers electrons as particles as well as waves, and Heisenberg's uncertainty principle according to which it is not possible to find out position and momentum of a small particle such as electron with absolute accuracy.

In this chapter, we shall be discussing these modern principles.

1.1. DUAL NATURE OF RADIATION

Dual nature of light was proposed by Einstein in 1905. He suggested that light can behave a particle as well as wave. Some of the phenomena of light could be explained by considering light to be a stream of particles while there are some experimental observations which can be explained by wave nature of light. Let us take brief account of *particle as well as wave* nature of light and other forms of radiant energy.

1. Wave nature of radiation. One of the earlier attempt to explain the phenomena of light such as reflection, diffraction, interference, refraction, etc., was made by Huygen by suggesting wave character of light. However, in 1956, James Maxwell proposed that light and other radiation are transmitted and propagated through space continuously in the form of *electromagnetic waves**. These *waves* are so called because they

*Electromagnetic waves can be generated by the *to and fro* oscillations of a charged body or a magnet. Energy of these waves is directly proportional to their frequency. These waves do not require any medium for propagation and can be transmitted through space. Different types of electromagnetic radiations travel with the same velocity through space or air which is nearly equal to 3×10^8 ms^{-1}.

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are associated with electrical as magnetic fields acting perpendicular to the direction of their propagation. Hence, they are also called **electromagnetic radiation**. The energy associated with a radiation is directly proportional to its intensity and therefore, radiation of any frequency can have any amount of energy depending upon its intensity.

Limitation of wave theory of radiation

Though the wave theory of radiation could successfully explain the phenomena of interference and diffraction, it failed to explain the phenomena of photoelectric effect and black body radiation. These phenomena could be explained only by considering that radiations possess dual nature, *i.e.*, wave nature as well as particle nature.

(*a*) **Black body radiation.** An ideal black body is a perfect absorber and perfect emitter of radiation. When such a body is heated it becomes red hot. In other words, it emits red coloured light. As the temperature is further increased, the colour of the radiation emitted changes from red to yellow to white and finally to purple. This implies that wave length of radiation emitted by black body changes gradually. These observation could not be explained by classical wave theory. According to this theory, wavelength of emitted radiation should have remained the same, however intensity might have changed with rise in temperature.

(*b*) **Photoelectric Effect.** It is observed that electrons are ejected from surface of certain metals when light falls on it. This is known as photoelectric effect. Thus, ***photoelectric effect may be defined as the phenomenon of ejection of electrons from the surface of a metal when light of suitable frequency strikes it.*** The electrons, thus, ejected are called **photoelectrons.**

It must be noted here that the photoelectric effect is shown by any metal in a photoelectric cell only. The apparatus showing the photoelectric effect is given in Fig. 1.1. It comprises an evacuated tube with metal having low ionisation energy and constituting the negative electrode. Now when light of sufficiently high energy strikes the metal, electrons are knocked off from its surface and move towards the positive electrode. These electrons constitute a current flowing through the circuit.

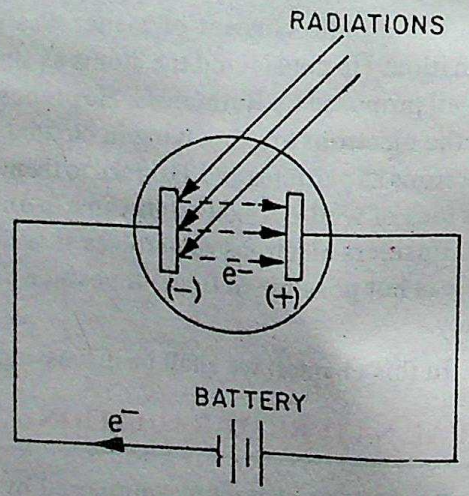

Fig. 1.1. Photoelectric Effect.

Only a few metals show this effect under the action of visible light but many more can show it under the action of more energetic ultraviolet light. Caesium with lowest I.E. emits electrons very easily.

Some important observations about photoelectric effect are :

(*i*) For a particular metal, there exists a threshold frequency such that, at frequencies below the threshold, no electrons are emitted, no matter how large the intensity is or how long the irradiation occurs.

(*ii*) The maximum kinetic energy of photoelectrons is directly proportional to the frequency of the incident radiation but is independent of its intensity. [Fig. 1.2 (*a*) and (*b*)].

(*iii*) The number of photoelectrons emitted per second is directly proportional to the intensity of the incident radiation but does not depend upon its frequency.

These observations could not be explained on the basis of wave theory according to which the energy of light depends upon its intensity and not frequency. Thus, light of any frequency can be made to have

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sufficient energy to cause the emission of electrons merely by increasing its intensity. Moreover, in that case the energy of the ejected electrons should be proportional to the intensity of light.

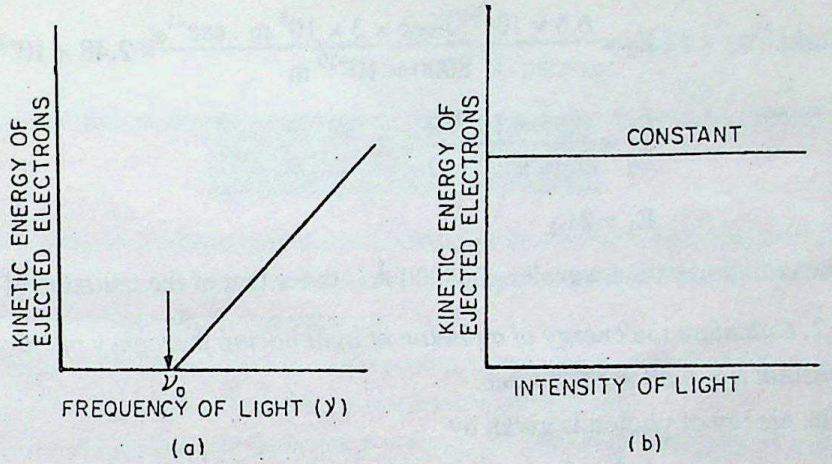

Fig. 1.2. Dependence of kinetic energy of photoelectron on frequency and intensity of incident radiation.

2. Particle Nature and Planck's Quantum Theory of Radiation. The failure of the classical electromagnetic theory of radiation to explain the phenomenon of photoelectric effect led Max Planck (1901) to propose a new theory known as **Quantum theory of radiation.** The main points of this theory are :

1. ***Radiant energy is emitted or absorbed not continuously but dicontinuously in the form of small packets of energy called quanta.***

Each wave packet or **quantum** is associated with definite amount of energy. *In case of light, the quantum of energy is often called* **photon.**

2. ***The amount of energy associated with a quantum of radiation is proportional to the frequency of radiation.***

$$E \propto \nu$$

or

$$\mathbf{E = h\nu}$$

where h is a constant known as **Planck's constant** and is equal to $\mathbf{6.625 \times 10^{-34}}$ **joule-sec.**

The energy of a photon of light in terms of wavelength λ and velocity of light c, is given as

$$E = h\nu$$

$$E = h\frac{c}{\lambda} \qquad (\because \ c = \nu\lambda; \quad \nu = c/\lambda)$$

3. ***A body can emit or absorb energy only in terms of the integral multiples of quantum, i.e.,***

$$E = nh\nu$$

where $n = 1, 2, 3, 4, ...$

This means that a body can emit or absorb energy as $h\nu$, $2h\nu$, $3h\nu$, $4h\nu$ ..... but it cannot emit or absorb energy in fractional values of $h\nu$ such as $1.5h\nu$ or $2.5h\nu$.

Example 1.1. *Calculate and compare the energies of two radiations, one with a wavelength of 4000 Å and the other with 8000 Å.*

Solution. $E = h\nu = h \times \frac{c}{\lambda}$

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$$E_1 = \frac{6.6 \times 10^{-34} \text{ J-sec} \times 3 \times 10^8 \text{ m . sec}^{-1}}{4000 \times 10^{-10} \text{ m}} = 4.95 \times 10^{-19} \text{ J}$$

$$E_2 = \frac{6.6 \times 10^{-34} \text{ J-sec} \times 3 \times 10^8 \text{ m . sec}^{-1}}{8000 \times 10^{-10} \text{ m}} = 2.48 \times 10^{-19} \text{ J}$$

$$\frac{E_1}{E_2} = \frac{4.95 \times 10^{-19} \text{ J}}{2.48 \times 10^{-19} \text{ J}} = 2$$

or $$\mathbf{E_1 = 2E_2}$$

Energy of the radiation with a wavelength 4000 Å is twice that of the radiation of wavelength 8000 Å.

Example 1.2. *Calculate the energy of a photon of light having frequency of 1.0×10^{15} sec^{-1}. Planck's constant $h = 6.63 \times 10^{-34}$ J-sec.*

Solution. The energy of photon is given by

$$E = h\nu$$

Frequency ν is given to be $= 1.0 \times 10^{15}$ sec^{-1}

and Planck's constant $h = 6.63 \times 10^{-34}$ J-sec

$$E = 6.63 \times 10^{-34} \text{ J-sec} \times 1.0 \times 10^{15} \text{ sec}^{-1} = \mathbf{6.63 \times 10^{-19}\ J.}$$

Example 1.3. *3×10^{18} photons of a certain light radiation are found to produce 1.5 J of energy. Calculate the wavelength of light radiations ($h = 6.63 \times 10^{-34}$ J-sec).*

Solution. The energy of a photon is given as

$$E = h\nu$$

∴ Energy of N of photons is

$$E = N\,h\nu = Nh\frac{c}{\lambda}$$

or $$\lambda = \frac{Nhc}{E}$$

$$= \frac{3 \times 10^{18} \times 6.63 \times 10^{-34} \text{ J-sec} \times 3 \times 10^8 \text{ m . sec}^{-1}}{1.5 \text{ J}} = 39.78 \times 10^{-8} \text{ m}$$

$$= 39.78 \times 10^{-8} \times 10^{10} \text{ Å}$$

$$= \mathbf{3978\ Å.} \qquad [\because\ 1 \text{ m} = 10^{10} \text{ Å}]$$

Example 1.4. *A 100 watt bulb is emitting monochromatic light having wavelength 6000 Å. Calculate the number of photons emitted by the bulb in one minute.*

Solution. 100 watt means the bulb is emitting 100 Joules per second.

Energy emitted in one minute $= 100 \times 60$ J

$= 6000$ J

Now energy of photon is given by the relation,

$$E = h\nu$$

$$= \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \text{ Js} \times 3 \times 10^8 \text{ ms}^{-1}}{6000 \times 10^{-10} \text{ m}} = 3.31 \times 10^{-19} \text{ J}$$

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$$\text{Number of photons emitted per minute} = \frac{\text{Energy emitted per minute}}{\text{Energy per photon}}$$

$$= \frac{6000 \text{ J}}{3.31 \times 10^{-19} \text{ J/photon}} = 1.81 \times 10^{22} \text{ photons.}$$

REVIEW PROBLEMS

1.1. Calculate the minimum amount of energy that can be emitted or absorbed at the frequency 3×10^{15} Hz.

1.2. Calculate the energy of one mole photons of a radiation having wavelength 3000 Å.

1.3. Calculate the wavelength of a photon having energy 2 eV.

1.4. Calculate the frequency and wavelength in Å of a photon having energy equal to 2 eV.

1.5. Calculate the energy of a photon of radiation having wavelength 100 nm.

1.6. Calculate the number of photons of a light with wavelength of 400 nm that can provide 2 joule of energy.

1.7. A line in the visible region of the spectrum is found to occur at 500 nm. Calculate the decrease in energy as this photon is emitted ? $h = 6.63 \times 10^{-34}$ J-sec.

1.8. A certain photochemical reaction is found to require 8.1×10^{-19} J energy per water molecule. Calculate the number of photons (per water molecule) of light with wavelength of 2.21×10^{-6} m that is required to initiate the reaction.

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Explanation of Photoelectric Effect

It was Einstein who explained the photoelectric effect on the basis of quantum theory. According to him electrons in metals are held by some attractive forces. To overcome these forces certain minimum amount of energy is required which is characteristic of the metal. This is called **photoelectric work function.** Now to cause ejection of electrons, the photons of incident light should have energy equal to or greater than this work function. We know from the quantum theory that energy of photon is directly proportional to frequency of the radiation. So the incident photons should have certain minimum frequency called **threshold frequency or critical frequency** (ν^0).

$$h\nu^0 = \text{Photoelectric work function.}$$

If frequency of the incident photon is less than ν^0, the energy of photon will be less than the minimum energy required to eject the electrons and hence no electrons would be ejected no matter what the intensity of the radiation is or for how long the irradiation occurs. If the photon has energy more than the energy required to remove the electron then each such photon of light on its collision with the electron at the surface disappears to overcome the binding energy of the electron. The excess energy is taken up by the electron as its kinetic energy. This may be written as

Energy of the striking photon = Energy required to eject electron + Kinetic energy of the photoelectron

or

$$h\nu = h\nu^0 + \text{K.E.}$$

$$\text{K.E.} = h\nu - h\nu^0 = h(\nu - \nu^0)$$

The validity of the above expression was tested by Millikan by calculating the value of h. It was found to be 6.57×10^{-34} J-s, which is in agreement with actual value of 6.626×10^{-34} J-s.

Since for a particular metal ν^0 and h are constants, so kinetic energy of photoelectrons is directly proportional to frequency. Kinetic energy of photoelectrons is independent of intensity because increase in intensity does not effect the energy of photons rather it simply increases the number of photons falling on the surface of metal and hence increases the number of photoelectrons.

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The photoelectric effect supports the particulate nature of light because only a light of suitable frequency and not of any frequency can bring about the emission of photoelectrons. Also, increasing the frequency of radiation increases the velocity of electrons whereas increasing the intensity does not change it.

Dual Nature of Radiations. As described above, the photoelectric effect could be explained considering that radiations consist of small packets of energy called quanta or quantums. These packets of energy can be treated as *particles*. On the other hand, radiations exhibit phenomena of interference and diffraction which indicate that they possess *wave nature*. So it may be concluded that *radiations possess dual nature, i.e.*, particle nature as well as wave nature. Einstein (1905) even calculated the mass of the photon associated with a radiation of frequency ν as given below :

The energy E of the photon is given as

$$E = h\nu \qquad ...(i)$$

Also according to Einstein's equation,

$$E = mc^2 \qquad ...(ii)$$

where m is the mass of photon.

From equations (*i*) and (*ii*), we get

$$h\nu = mc^2$$

$$\boxed{m = \frac{h\nu}{c^2}} \qquad ...(iii)$$

$$m = \frac{h}{c^2} \cdot \frac{c}{\lambda} \qquad \left(\because \nu = \frac{c}{\lambda}\right)$$

$$\boxed{m = \frac{h}{c\lambda}} \qquad ...(iv)$$

Equations (*iii*) and (*iv*) can be used to calculate the mass of the photon.

Example 1.5. *The minimum energy required for the photoemission of electron from the surface of a metal is 4.95×10^{-19} Joules. Calculate the critical frequency and the corresponding wavelength of the photon required to eject the electron.*

Solution. Minimum energy required for the emission of electrons = 4.95×10^{-19} Joules.

Let the critical frequency of the photon to eject the electron be ν sec^{-1}

We know $E = h\nu$

or $\nu = \frac{E}{h}$

$$\therefore \quad \nu = \frac{4.95 \times 10^{-19}\ J}{6.6 \times 10^{-34}\ J\text{-}s} = 7.5 \times 10^{14}\ s^{-1}$$

Also $$\lambda = \frac{c}{\nu} = \frac{3 \times 10^8\ ms^{-1}}{7.5 \times 10^{14}\ s^{-1}} = 4 \times 10^{-7}\ m.$$

Example 1.6. *Calculate the mass of a photon of sodium light having wavelength 5894 Å and velocity, $3 \times 10^8\ ms^{-1}$, $h = 6.6 \times 10^{-34}\ kg\ m^2\ s^{-1}$.* (P.S.E.B. 1992)

Solution. Wavelength of photon, $\lambda = 5894$ Å $= 5894 \times 10^{-10}$ m

Velocity of light, $c = 3 \times 10^8\ m\ s^{-1}$

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Mass of photon $= \frac{h}{c\lambda}$

$$= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{3 \times 10^8 \text{ m s}^{-1} \times 5894 \times 10^{-10} \text{ m}} = 3.7 \times 10^{-36} \text{ kg.}$$

REVIEW PROBLEMS

1.9. Light of wavelength 400 nm strikes a certain metal which has a photoelectric work function of 2.13 eV. Find out the kinetic energy of the most energetic photoelectron.

1.10. The threshold frequency for the ejection of electrons from potassium metal is 5.3×10^{14} s^{-1}. Will the photon of a radiation having energy 3.3×10^{-19} J exhibit photoelectric effect ?

1.11. The critical wavelength for emitting photoelectrons from a metal is 6×10^3 Å. What should be the wavelength of radiation to produce photoelectrons having twice the kinetic energy of those produced by radiation of wavelength 3×10^3 Å ?

1.12. The minimum energy required for the photoemission of electrons from the surface of a metal is 4.95×10^{-19} J. Find the K.E. of most energetic photoelectrons when the metal is irradiated with radiation of wavelength of 3000 Å.

1.13. The energy required to remove an electron from the surface of sodium metal is 2.3 eV. What is the longest wavelength of radiation with which it can show photoelectric effect ?

1.14. If a light with frequency of 4.0×10^{16} Hz emitted photoelectrons with double the kinetic energy as are emitted by the light of frequency 2.5×10^{16} Hz from the same metal surface then what is the threshold frequency of the metal ?

1.15. If the critical wavelength for producing photoelectric effect is 2000 Å, then what wavelength of light will be required to produce photoelectrons with double the kinetic energy of those produced by light of wavelength = 1500 Å ?

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1.2. DUAL NATURE OF MATTER—de Broglie Equation

Louis de Broglie (1924) proposed that just as radiations have particle nature, the material particles are also associated with wave nature. He also gave a relation for calculating the wavelength of the wave associated with a particle of mass m moving with velocity v as given below :

$$\lambda = \frac{h}{mv}$$

Derivation of de Broglie Relationship

The energy E of a photon of frequency v is given by

$$E = h\nu \quad \text{...(i)}$$

Also according to Einstein's equation,

$$E = mc^2 \quad \text{...(ii)}$$

where m is the mass of photon.

From equations (*i*) and (*ii*), we get

$$mc^2 = h\nu$$

$$mc^2 = h \cdot \frac{c}{\lambda} \qquad \left(\because \nu = \frac{c}{\lambda}\right)$$

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Rearranging, we get $\lambda = \frac{h}{mc}$.

de Broglie pointed out that the same equation might be applied to material particle by using m for the mass of the particle instead of the mass of photon and replacing c, the velocity of the photon, by v, the velocity of the particle.

$$\boxed{\lambda = \frac{h}{mv}} \quad ...(iii)$$

Equation (*iii*) is called de Broglie's equation. It may also be written as

$$\boxed{\lambda = \frac{h}{p}} \quad ...(iv)$$

where p is the momentum of the particle.

The waves associated with material particles or objects in motion are called **matter waves** or **de Broglie waves.** These waves are distinctively different from the electromagnetic waves. The differences between the two are summarised in Table 1.1.

Table 1.1. Distinction Between Electromagnetic Waves and Matter Waves

Electromagnetic Waves	*Matter Waves*
1. These waves are associated with electrical and magnetic fields.	1. These waves are not associated with electrical and magnetic fields.
2. Electromagnetic waves can be emitted or radiated in space.	2. Matter waves are neither radiated into space nor emitted by the particles. These are simply associated with the particles.
3. All electromagnetic waves travel with the same velocity.	3. Matter waves travel with different velocities.
4. The velocity of all electromagnetic waves is equal to that of light (3.0×10^8 ms^{-1}).	4. The velocity of matter waves is different from that of light.
5. The wavelength of electromagnetic waves is given by $\lambda = c/v = h/mc$.	5. The wavelength of matter waves is given $\lambda = h/mv = h/p$.

Significance of de Broglie Waves

The wave character puts some restriction on how precisely we can express the position of an electron or any other small moving particle. This is due to the reason that unlike particles, waves do not occupy a well defined position in space and are delocalised. The wave nature of matter, however, has no significance for objects of ordinary size because wavelength of the wave associated with them is too small to be detected. For example, a ball of mass 1.0 kg moving with a velocity 1.0 m/sec is associated with a wave of wavelength 6.62×10^{-34} m which is too small to be detected.

$$\lambda = \frac{h}{mv} = \frac{6.62 \times 10^{-34} \text{ kg m}^2 \cdot \text{s}^{-1}}{1.0 \text{ kg} \times 1.0 \text{ m s}^{-1}}$$

$$= 6.62 \times 10^{-34} \text{ m} = \mathbf{6.62 \times 10^{-22}} \text{ pm.}$$

Therefore, such bodies have predominently particle character. Wave nature of such bodies is insignificant. On the other hand, microscopic or submicroscopic particles like electrons are associated with matter waves of observable length. For example, an electron moving with a velocity of 6.0×10^6 m/sec is associated with a wave of wavelength 1.21×10^{-10} m (121 pm).

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$$\lambda = \frac{h}{mv}$$

$$= \frac{6.62 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{9.1 \times 10^{-31}\ \text{kg} \times 6.0 \times 10^{6}\ \text{ms}^{-1}} = 1.21 \times 10^{-10}\ \text{m} = \mathbf{121\ pm.}$$

Thus, it is quite evident that, *de-Broglie concept is more significant for microscopic or sub-microscopic particles whose wavelength can be measured.*

Verification of Dual Nature of Electrons

1. Wave Character. Louis de Broglie's concept of wave character of electrons was experimentally verified by **Davisson and Germer**. They subjected a stream of electrons emitted from a tungsten filament to the influence of strong electrical field so as to accelerate the speed of the electrons. When these electrons were made to strike against nickel crystal as grating, concentric dark and bright rings were formed on the screen (Fig. 1.3). This diffraction pattern of electrons by crystal was similar to that observed for X-rays. Since X-rays have wave character, therefore, *the electrons must also have wave character associated with them.* Moreover, the wavelengths of the electrons determined by the diffraction experiments were found to be in agreement with the values calculated from de Broglie's equation.

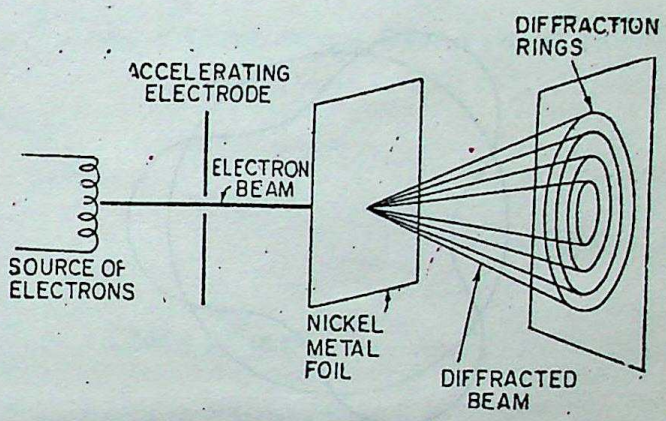

Fig. 1.3. Electron diffraction experiment by Davisson and Germer.

2. Particle Character. The particle nature of electrons is illustrated as follows. If an electron strikes a screen coated with zinc sulphide, it produces a spot of light known as **scintillation** ; one electron producing only one scintillation point. This means that the scintillation and, as such, the striking electron must be localised and not spread out like a wave. In other words, this suggests that an electron behaves like a particle. From the above discussion, it is clear that electrons possess dual nature, *i.e.*, wave character as well as particle character.

de Broglie's concept of dual nature of matter finds application in the *construction of electron microscope* and *the study of surface structure of solids by electron diffraction.*

The de Broglie equation applies not only to electrons but also to other small moving material objects such as neutrons, protons, atoms, molecules, etc.

To have a more clear picture about a wave and a particle, the differences between the two are tabulated below :

Wave	*Particle*
1. A wave is delocalised in space.	1. A particle is a localised point in space.
2. Two or more waves can simultaneously exist at a given region in space.	2. More than one particle cannot be present at a given position in space.
3. The two waves in the same region may undergo constructive or destructive interference.	3. The two particles in same region in space cannot show the phenomenon of interference.

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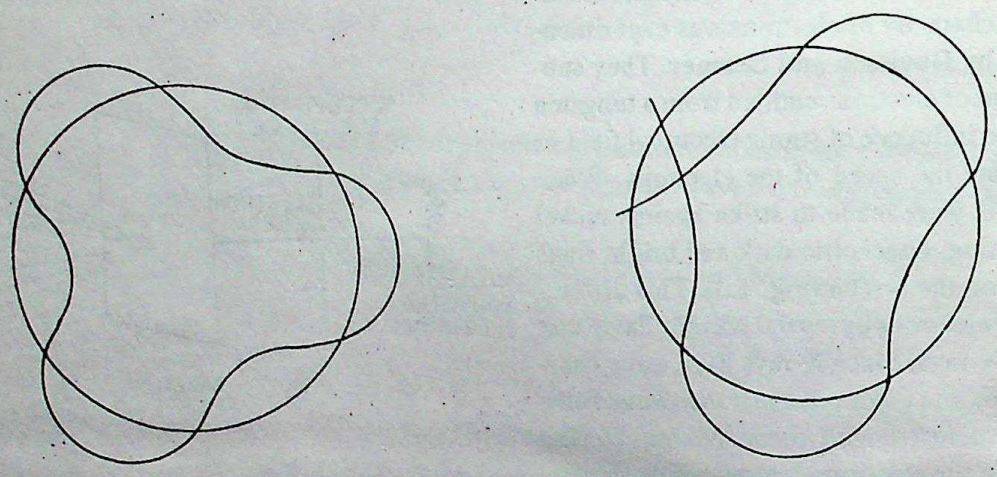
Derivation of Bohr's postulate of quantisation of angular momentum from de-Broglie equation. According to Bohr's model only those circular orbits are permitted in which angular momentum of the electron is integral multiple of $h/2\pi$, *i.e.*,

$$mvr = n\frac{h}{2\pi}.$$

According to de Broglie concept, the electrons are not only particles but also have wave character associated with them. Therefore, for the wave to be completely in phase, the circumference of the orbit should be integral multiple of wavelength λ.



(*a*) (*b*)

Fig. 1.4. (*a*) Wave in phase (*b*) Wave out of phase.

Therefore, $2\pi r = n\lambda$

where, r is the radius of the orbit and n is an integer.

But from de Broglie equation we know that

$$\lambda = \frac{h}{mv}$$

$$\therefore \quad 2\pi r = n \cdot \frac{h}{mv}$$

$$\boxed{mvr = n\frac{h}{2\pi}}$$

Example 1.7. *Calculate the wavelength of a body of mass 1 mg moving with a velocity of 10 m sec^{-1}.*

Solution. We know, $\lambda = \frac{h}{mv}$

Substituting the values,

$$m = 1 \text{ mg} = 10^{-6} \text{ kg}$$

$$v = 10 \text{ m sec}^{-1}$$

and

$$h = 6.625 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}$$

$$\lambda = \frac{6.625 \times 10^{-34}}{10^{-6} \times 10} = 6.625 \times 10^{-29} \text{ m.}$$

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Example 1.8. *Calculate the momentum of a moving particle which has a de Broglie wavelength of 200 pm.*

Solution. We know, $\lambda = \frac{h}{mv}$ or $mv = \frac{h}{\lambda}$

$$h = 6.62 \times 10^{-34}\ \text{Js} = 6.62 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}$$

$$\lambda = 200\ \text{pm} = 2 \times 10^{-10}\ \text{m}$$

Momentum, $$mv = \frac{6.62 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{2 \times 10^{-10}\ \text{m}} = \mathbf{3.31 \times 10^{-24}\ kg\ m\ s^{-1}}.$$

Example 1.9. *A moving electron has 5×10^{-25} Joules of kinetic energy. What is the de Broglie wavelength ?*

Solution. Mass of the electron $m = 9.1 \times 10^{-31}$ kg

$$\text{K.E.} = \tfrac{1}{2} mv^2 = 5 \times 10^{-25}\ \text{J}$$

$$\tfrac{1}{2} \times 9.1 \times 10^{-31}\ \text{kg} \times v^2 = 5 \times 10^{-25}\ \text{J}$$

$$v = \sqrt{\frac{2 \times 5 \times 10^{-25}}{9.1 \times 10^{-31}}} = 1.048 \times 10^3\ \text{m s}^{-1}.$$

$$h = 6.62 \times 10^{-34}\ \text{Js} = 6.62 \times 10^{-34}\ \text{kg m s}^{-1}$$

or $$\lambda = \frac{h}{mv}$$

$$= \frac{6.62 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{9.1 \times 10^{-31}\ \text{kg} \times 1.048 \times 10^3\ \text{m s}^{-1}} = \mathbf{6.94 \times 10^{-7}\ m.}$$

Example 1.10. *An electron beam is accelerated by a potential difference of 10000 volts. What is the wavelength of the wave associated with the electron beam ? Mass of electron = 9.1×10^{-31} kg.*

Solution. Kinetic energy of the electron = 10000 eV

$$= 10000 \times 1.602 \times 10^{-19}\ \text{J} = 1.602 \times 10^{-15}\ \text{J}$$

Velocity of electron can be calculated from kinetic energy as follows :

$$\tfrac{1}{2} mv^2 = 1.6 \times 10^{-15}\ \text{J}$$

$$= 1.6 \times 10^{-15}\ \text{kg.m}^2.\text{s}^{-2}$$

$$v = \sqrt{\frac{2 \times 1.6 \times 10^{-15}\ \text{kg m}^2\text{s}^{-2}}{9.11 \times 10^{-31}\ \text{kg}}}\quad v = 5.9 \times 10^7\ \text{m s}^{-1}$$

Now we know from de Broglie equation

$$\lambda = \frac{h}{mv}$$

$$= \frac{6.62 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{9.1 \times 10^{-31}\ \text{kg} \times 5.9 \times 10^7\ \text{m s}^{-1}}$$

$$= 0.123 \times 10^{-10}\ \text{m} = \mathbf{0.123\ Å.}$$

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REVIEW PROBLEMS

1.16. Calculate the momentum of a particle which has wavelength of 2 Å. $h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}. *[CBSE (1) 1992]*

1.17. Calculate the wavelength of a particle of mass $m = 6.6 \times 10^{-27}$ kg moving with kinetic energy 7.425×10^{-13} J. ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}) *(H.P. Board 1993)*

1.18. Calculate the wavelength of a 100 kg rocket moving with a velocity of 300 km per hour ($h = 6.62 \times 10^{-34}$ Js).

1.19. Calculate the momentum of a particle with a de Broglie wavelength of 1 Å.

1.20. What must be the velocity of a beam of electrons if they are to display a de Broglie wavelength of 1 Å.

1.21. Calculate the wavelength of an electron moving with a velocity of 10^3 ms^{-1} ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1} ; Mass of electron = 9.1×10^{-31} kg). *[CBSE 1992]*

1.22. A beam of α-particles moves with a velocity of 3.28×10^3 m/s. Calculate the wavelength of the α-particles.

1.23. Calculate the de Broglie wavelength of a stone of mass 10 g, moving with a velocity of 2×10^2 m s^{-1}. ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}) *[Har. (Sc) 1992]*

1.24. An electron is moving with a kinetic energy of 4.55×10^{-25} Joule. Calculate de Broglie wavelength for it. (Mass of electron = 9.1×10^{-31} kg ; $h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}). *(CBSE 1993)*

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1.3. THE UNCERTAINTY PRINCIPLE

The position and the velocity of the bodies which we come across in our day-to-day life can be determined precisely at a particular moment of time. Hence, the paths or *trajectories* of such bodies can be predicted. However, in the case of small particles such as electrons it is impossible to determine simultaneously its position and velocity at a given instant with absolute certainty. Hence, it is not possible to talk of trajectory of an electron. Werner Heisenberg (1927) put forward this fact in the form of a well-known principle, called **Heisenberg's uncertainty principle.** This principle, which is a direct consequence of the dual nature of matter and radiation, states that.

It is impossible to measure simultaneously both the position and velocity (or momentum) of a microscopic particle with absolute accuracy or certainty.

Mathematically, uncertainty principle may be put as

$$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

where, Δx = uncertainty in position

Δp = uncertainty in momentum

h = Planck's constant.

The sign ≥, means that the product of Δx and Δp can be either greater than or equal to $\frac{h}{4\pi}$. It can never be less than $\frac{h}{4\pi}$. Since the minimum product of Δx and Δp is constant, it means that

$$\Delta x \propto \frac{1}{\Delta p}.$$

It follows, therefore, that if uncertainty in position (Δx) is less, then uncertainty in momentum (Δp) would be large. Similarly, if uncertainty in momentum (Δp) is less, the uncertainty in position (Δx) would be large.

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Now let us understand the physical picture of uncertainty principle. In order to observe the position of an object, light of some suitable wavelength is made to fall on the object which scatters light. Now when the scattered light enters our eye we can see the object. For scattering to take place, the wavelength of the light used should be of the same order as the size of the object. If the object is of reasonable size its position and velocity will not change by the impact of the light radiations. Thus, it is possible to know both the position and velocity of the object exactly.

In case of microscopic particles like electron, the impact of striking photon causes large displacement from the normal path. As a result, both the velocity and momentum of the particle change and send the electron in the unpredictable direction.

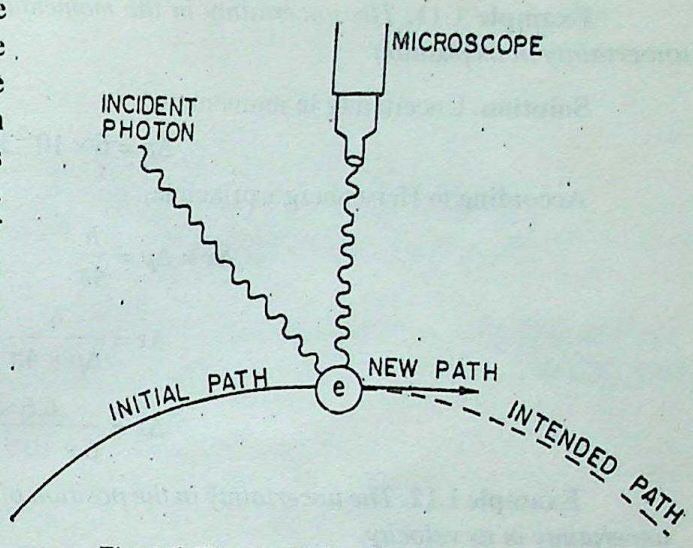

Fig. 1.5. The change in the path of electron by photon of light.

It can be shown that if λ is the wavelength of the radiation used to observe the particle then the position of the particle cannot be determined with accuracy greater than $\pm\lambda$. Therefore, in order to observe the position of the particle accurately, wavelength of the light used to observe it, should be as small as possible. However, we know that photons of radiations of smaller wavelength are associated with large amount of energy and therefore when such photons strike the particle these disturb the momentum of the particle to a greater extent *i.e.*, uncertainty in momentum increases. In order to determine momentum with less uncertainty we will use radiations of longer wavelengths, but in that case uncertainty in position would become large. It may, thus, be concluded that it is not possible to determine simultaneously both the position and momentum of a small moving particle such as electron with absolute accuracy or in other words, it implies that the position of electron cannot be known exactly as postulated by Bohr. Instead it is only possible to predict the probable region in a given space where we can find electron. ***Thus, Hiesenberg replaced the concept of definite orbits by the concept of probability.***

Uncertainty principle in our daily life. In our daily life uncertainty principle has no significance. In case of objects of ordinary size the uncertainties in position and momentum are very small as compared to the size of the object and the momentum of the object respectively. Hence these may be neglected. On the other hand, in the case of small microscopic particles uncertainties in position and momentum are of the same order as the actual size and momentum of the particle respectively. Hence these cannot be neglected.

Electron cannot be present in the Nucleus

Heisenberg's uncertainty principle can help us to establish that electron cannot be present in the nucleus of the atom.

The size of the nucleus of the order of 10^{-15} m. Now, if electron is to exist in nucleus then uncertainty in its position has to be 10^{-15} m.

Now, $\Delta x\, \Delta p = \dfrac{h}{4\pi}$ or $\Delta x \times m\Delta v = \dfrac{h}{4\pi}$

or $$\Delta v = \frac{h}{4\pi m \times \Delta x} = \frac{6.6 \times 10^{-34}}{4 \times 3.14 \times 9.1 \times 10^{-31} \times 10^{-15}} = 5.77 \times 10^{10}\ \text{ms}^{-1}$$

It is quite evident that value of Δv, the uncertainty in velocity is much higher than the velocity of light (3×10^8 ms^{-1}) which is not possible. Hence, electron cannot be present in atomic nucleus.

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Example 1.11. *The uncertainty in the momentum of a particle is 6×10^{-2} kg ms^{-1}. Calculate the uncertainty in its position.*

Solution. Uncertainty in momentum

$$\Delta p = 6 \times 10^{-2} \text{ kg m s}^{-1}$$

According to Heisenberg's principle,

$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

$$\therefore \quad \Delta x = \frac{h}{\Delta p \times 4\pi}$$

$$\Delta x = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{6 \times 10^{-2} \text{ kg m s}^{-1} \times 4 \times 3.14} = \mathbf{8.76 \times 10^{-34} \text{ m}}.$$

Example 1.12. *The uncertainty in the position of a moving bullet of mass 10 g is 10^{-5} m. Calculate the uncertainty in its velocity.*

Solution. Uncertainty in the position,

$$\Delta x = 10^{-5} \text{ m}$$

Mass of the bullet $m = 10 \text{ g} = 10 \times 10^{-3}$ kg

According to Heisenberg's principle,

$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

$$\Delta x \times m\Delta v = \frac{h}{4\pi} \qquad [\because \ \Delta p = m\Delta v]$$

$$\therefore \quad \Delta v = \frac{h}{4\pi} \times \frac{1}{\Delta x \times m}$$

$$= \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 10^{-5} \text{ m} \times 10 \times 10^{-3} \text{ kg}} = \mathbf{5.2 \times 10^{-28} \text{ ms}^{-1}}.$$

Example 1.13. *Calculate the product of uncertainty in position and velocity for an electron of mass 9.1×10^{-31} kg according to Heisenberg's uncertainty principle.*

Solution. According to Heisenberg's uncertainty principle,

$$\Delta x \times \Delta p = \frac{h}{4\pi}$$

$$\Delta x \times m\Delta v = \frac{h}{4\pi}$$

$$\Delta x \times \Delta v = \frac{h}{4\pi m}$$

$$\therefore \quad \Delta x \times \Delta v = \frac{6.6 \times 10^{-34} \text{ kg m}^2 \text{ s}^{-1}}{4 \times 3.14 \times 9.1 \times 10^{-31} \text{ kg}} = \mathbf{5.8 \times 10^{-5} \text{ m}^2 \text{ s}^{-1}}.$$

Example 1.14. *Calculate the uncertainty in the velocity of a cricket ball of mass 150 g, if the uncertainty in its position is of the order of 1 Å. ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1})* [CBSE (4) 1992]

Solution. Mass of ball, $m = 150$ g

$= 0.150$ kg

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Uncertainty in position, $\Delta x = 1\ \text{Å} = 10^{-10}\ \text{m}$

$$\Delta x \times m\Delta v = \frac{h}{4\pi}$$

$$\Delta v = \frac{h}{4\pi \times \Delta x \times m}$$

$$= \frac{6.6 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{4 \times 3.14 \times 10^{-10}\ \text{m} \times 0.150\ \text{kg}} = \mathbf{3.5 \times 10^{-24}\ m\ s^{-1}}.$$

Example 1.15. *The uncertainty in the position and velocity of a particle are 10^{-2} m and 5.27×10^{-24} m s^{-1} respectively. Calculate mass of the particle ($h = 6.626 \times 10^{-34}$ kg m^2 s^{-1}).* [P.S.E.B. 1991]

Solution. According to Heisenberg's uncertainty principle,

$$\Delta \times \Delta p = \frac{h}{4\pi}$$

$$\Delta x \times m\Delta v = \frac{h}{4\pi}$$

$$m = \frac{h}{4\pi \times \Delta x \times \Delta v} = \frac{6.626 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{4 \times 3.14 \times 10^{-2}\ \text{m} \times 5.27 \times 10^{-24}\ \text{m s}^{-1}}$$

$$= \mathbf{1.00 \times 10^{-9}\ kg.}$$

Example 1.16. *If the electron is to be located within 5×10^{-5} pm, what will be the uncertainty in its velocity ?*

Solution. If the electron is to exist within 5×10^{-5} pm, the uncertainty in its position cannot be more than 5×10^{-5} pm.

$\therefore$ Let $\Delta x = 5 \times 10^{-5} \times 10^{-10}\ \text{m} = 5 \times 10^{-15}\ \text{m}$

$$\Delta x\ .\ \Delta p \geq \frac{h}{4\pi}$$

$$\Delta x\ .\ m.\ \Delta v \geq \frac{h}{4\pi}$$

$$\Delta v \geq \frac{h}{4\pi \Delta x\ .\ m}$$

$$\geq \frac{6.62 \times 10^{-34}\ \text{kg m}^2\ \text{s}^{-1}}{4 \times 3.14 \times 5 \times 10^{-15}\ \text{m} \times 9.1 \times 10^{-31}\ \text{kg}}$$

$$\geq 1.16 \times 10^{10}\ \text{m}$$

REVIEW PROBLEMS

1.25. Calculate the uncertainty in position of an electron if the uncertainty in its velocity is 5.7×10^5 ms^{-1}. ($h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}; Mass of electron = 9.1×10^{-31} kg) *[CBSE (2) 1992]*

1.26. Calculate the uncertainty in the momentum of a particle if the uncertainty in its position is 6.6×10^{-32} m.

1.27. If an electron is to be located within 10 pm what will be uncertainty in its velocity.

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1.28. What is the uncertainty in velocity of an electron if the uncertainty in its position is 10^{-10} m ? Mass of the electron is 9.1×10^{-31} kg and $h = 6.6 \times 10^{-34}$ kg m^2 s^{-1}.

1.29. The uncertainty in the position of a bullet weighing 20 g is $\pm 10^{-4}$ m, calculate the uncertainty in its velocity.

1.30. An electron has a velocity of 300 ms^{-1} that is accurate to 0.01%. With what accuracy can we locate the position of this electron ?

1.31. Calculate the product of uncertainties of displacement and velocity of a moving electron having mass of 9.1×10^{-28} g. ($h = 6.6 \times 10^{-34}$ kg.m^2 . s^{-1}) *(CBSE 1993)*

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1.4. QUANTUM MECHANICAL MODEL OF ATOM

On the basis of de Broglie's hypothesis and Heisenberg's uncertainty principle a new model of atom was developed during 1920's. This model is known as **quantum mechanical model**. In this model behaviour of the electron in an atom is described by an equation known as the **Schrodinger wave equation**

$$\frac{\partial^2\psi}{\partial x^2} + \frac{\partial^2\psi}{\partial y^2} + \frac{\partial^2\psi}{\partial z^2} + \frac{8\pi^2 m}{h^2}(E - V)\psi = 0$$

where x, y and z are the three space co-ordinates,

m is mass of the electron,

h is the Planck's constant,

E is the total energy and V is the potential energy of the electron,

ψ (*Greek* letter *psi*) is amplitude of the electron wave and is called **wave function,**

and $\frac{\partial^2\psi}{\partial x^2}$ refers to the second derivative of ψ with respect to x only and so on.

The solutions of Schrodinger wave equation are known as wave functions. When Schrodinger wave equation is solved for hydrogen atom, several solutions are obtained. Out of which only certain solutions are permissible. Each permitted solution* or wave function corresponds to a definite energy state and is called **orbital**. Each orbital can be considered as quantum mechanical analog of the electron orbits as proposed by Bohr. The electron orbitals in atoms are called *atomic orbitals* while those in a molecule are called *molecular orbitals*. Since in an atom (or a molecule) only specific or definite energy states are permitted, it implies that an electron in an atom (or a molecule) can have only certain specific values of energy. In other words, energy of electron in an atom is quantised.

This may also lead us to conclude on the basis of wave mechanical concepts that definite energy levels are present in an atom.

Significance of ψ

As a moving electron is associated with a wave and a wave is completely defined by its amplitude, therefore ψ refers to the amplitude of electron wave. It has got no physical significance. However, the square of ψ *i.e.*, ψ^2 has a physical significance. Just like light radiations where square of amplitude gives the intensity of light, similarly, in electron wave, ψ^2 gives the intensity of *electron at any point*. In other words, the knowledge of ψ^2 is helpful in assessing the probability of electron in a particular region. Thus ψ^2 is called **probability density** and ψ is referred to as **probability amplitude.**

*The permitted solutions of wave equation are also called as eigen functions.

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1.5. QUANTUM NUMBERS

In an atom a large number of electron orbitals are permissible. These orbitals are designated by a set of numbers known as quantum numbers. In order to specify energy, size, shape and orientation of the electron orbital, three quantum numbers are required. These are principal quantum number, azimuthal quantum number and magnetic quantum number. These follow directly from solutions of Schrodinger wave equation. In order to designate the electron, an additional quantum number called spin quantum number is needed to specify spin of the electron. ***Thus, each orbital in an atom is designed by a set of three quantum numbers and each electron is designated by a set of four quantum numbers.*** These quantum numbers are discussed below :

1. The Principal Quantum Number (n)

This is the most important quantum number as it determines to a large extent the energy of an electron. It also determines the average distance of an electron from the nucleus. It is denoted by the letter *n*. It can have any whole number value such as 1, 2, 3, 4, etc. The energy levels or energy shells corresponding to these numbers are designated as K, L, M, N*, etc. As the value of *n* increases, the electron gets farther away from the nucleus and its energy increases. The higher the value of *n*, the higher is the electronic energy.

The energy of the electron in hydrogen atom is given by the relation,

$$E_n = -k^2 \frac{2\pi^2 me^4}{n^2h^2}$$

where m = Mass of the electron

e = Charge on the electron

h = Planck's constant

n = Principal quantum number

k = A universal constant = 9.0×10^9 J.m/C^2.

The constant k is equal to inverse of the permittivity factor of the medium.

Substituting the values of π, m, e, h and k in the above energy expression, we get

$$E_n = -\frac{2.178 \times 10^{-18}}{n^2} \text{ J/atom}$$

or

$$E_n = -\frac{1.312 \times 10^3}{n^2} \text{ kJ/mole.}$$

According to the equation for E_n, the largest negative value of energy is obtained when n has the smallest permitted value, *i.e.*, when n is 1.

Thus, $n = 1$ gives the lowest energy state (E_1), of the electron in hydrogen atom. This state is called the *ground state* of the electron in the atom. For hydrogen atom, all other states with $n > 1$ are called *excited states*. The possible energy states of electron in hydrogen atom are :

$$E_1 = -1.312 \times 10^3 \text{ kJ mol}^{-1} \text{ when } n = 1$$

$$E_2 = -3.28 \times 10^2 \text{ kJ mol}^{-1} \text{ when } n = 2$$

$$E_3 = -1.46 \times 10^2 \text{ kJ mol}^{-1} \text{ when } n = 3$$

Thus, it is clear that the electron in hydrogen atom can have only certain specific values of energy.

Expression of Energy for hydrogen like Ions

For other hydrogen like species such as He^+, Li^{2+}, etc., the energy of the electron in various energy levels is given by the relation

*The letter notations come from experiments in spectroscopy and with X-rays.

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$$E_n = -k^2 \frac{2\pi^2 me^4 Z^2}{n^2 h^2}$$

where, Z is the atomic number of the atom. For He^+, the value of Z = 2.

2. The Angular Momentum Quantum Number or Azimuthal Quantum Number (l)

This quantum number is related to the orbital angular momentum of the electron. This is denoted by *l*. In fact, the orbital angular momentum of electron is given by the following expression

$$\textit{Orbital angular momentum} = \frac{h}{2\pi}\sqrt{l(l+1)},$$

where *l* is azimuthal quantum number.

The value of *l* gives the **sub-level** or **sub-shell** in which the electron is located. *It also determines the shape of the orbital* in which the electron is located. The number of sub-shells within a principal shell is determined by the value of *n* for that principal energy level. *Thus, l may have all possible whole number values from 0 to n – 1* for each principal energy level. The various sub-levels are designated* as *s, p, d, f* depending upon the value of *l*, as shown below :

Value of l →	0	1	2	3	4
Designation of the sub-shell →	*s*	*p*	*d*	*f*	*g*

For n = 1, *l* can have only one value, *i.e.*, 0. It means that an electron in first energy level can be present only in *s*-sub-shell (*l* = 0).

So **first energy level** has only **one-sub-shell**, *i.e.*, 1*s*.

For n = 2, *l* can have values 0 and 1. It means that the electron in second principal energy level may be located either in *s*-sub-shell (*l* = 0) or *p*-sub-shell (*l* = 1).

So, **second energy level** have only **two sub-shells**, *i.e.*, 2*s* and 2*p*.

For n = 3, possible values of *l* are 0, 1 and 2. This implies that an electron in third principal energy level may be present either in *s*-sub-shell (*l* = 0) or *p*-sub-shell (*l* = 1) or *d*-sub-shell (*l* = 2).

So **third energy level** has **three sub-shells**, *i.e.*, 3*s*, 3*p* and 3*d*. Similarly, **fourth energy level** (*n* = 4) can have **four sub-shells** ; 4*s*, 4*p*, 4*d* and 4*f*

It may be noted that in any main level, the order of energies of various sub-levels is

$$s < p < d < f.$$

3. The magnetic Quantum Number (m)

This quantum number is denoted by *m* and refers to the different orientations of electron cloud in a particular sub-shell. These different orientations are called **orbitals**. The number of orbitals in a particular sub-shell within a principal energy level is given by the number of values allowed to *m*, which in turn depend on the value of *l*. The possible values of *m* are all integral values from + *l* through 0 to – *l*, thus, making a total of (2*l* + 1) values.

For *l* = 0 (*i.e.*, *s*-sub-shell), *m* can have only one value, *m* = 0. It means that **s-sub-shell has only one orbital.**

For *l* = 1 (*i.e.*, *p*-sub-shell), *m* can have three values, +1, 0, and –1. This implies that **p-sub-shell has three orbitals.**

For *l* = 2 (*i.e.*, *d*-sub-shell), *m* can have five values +2, +1, 0, –1, –2. It means that **d-sub-shell has five orbitals.**

*These are spectroscopic terms, *s* means **sharp**, *p* means **principal**, *d* means **diffuse** and *f* means **fundamental**.

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For $l = 3$ (*i.e.*, *f*-sub-shell), m can have seven values +3, +2, +1, 0, –1, –2, –3. Hence, the *f*-sub-shell has **seven orbitals.**

The relationship between the principal quantum number (n), angular momentum quantum number (l) and magnetic quantum number (m) is summer in Table 1.2.

Table 1.2. Relationship among Values of n, l and m

Energy level	*Principal quantum number* (n)	*Possible values of* (l)	*Designation of sub-shell*	*Possible values of* (m)	*Number of orbitals*	
					In a given sub-shell ($2l + 1$)	*In a given energy level* (n^2)
K	1	0	1*s*	0	1	1
L	2	0	2*s*	0	1	4
		1	2*p*	+ 1, 0, – 1	3	
M	3	0	3*s*	0	1	9
		1	3*p*	+ 1, 0, – 1	3	
		2	3*d*	+ 2, + 1, 0, – 1, – 2	5	

4. The Spin Quantum Number

This quantum number which is denoted by s does not follow from the wave mechanical treatment but arises from the spectral evidence that electron in its motion about the nucleus also rotates or spins about its own axis. The spin of electron produces a small magnetic field as a result of which it behaves as a small tiny magnet. The spin quantum number ; in fact, describes the spin orientation of the electron. It is designated by s.

The electron spin can be either clockwise or anti-clockwise. The spin quantum number can have only two values which are $+\frac{1}{2}$ and $-\frac{1}{2}$. The $+\frac{1}{2}$ value indicates clockwise spin (generally represented by an arrow pointing upwards, *i.e.*, ↑) and $-\frac{1}{2}$ indicates anti-clockwise spin (generally represented by an arrow pointing downwards, *i.e.*, ↓). It may be noted that values of spin quantum number are independent of the values of other three quantum numbers.

Although this half integer value is in contradiction to integral multiple rule of quantisation of angular momenta but the use of half integer for s, leads to results which are in complete agreement with experimental facts. Further, the wave mechanical approach also provides a theoretical justification. A further discussion is beyond the scope of the present text.

Example 1.17. *Energy of the electron in hydrogen atom is given by the expression,*

$$E_n = -\frac{1.312 \times 10^6}{n^2} J\ mol^{-1}$$

(*a*) *Calculate the amount of energy required to promote electron from the first energy level to the third energy level.*

(*b*) *What will be the ionisation energy of hydrogen ?*

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Solution. (*a*) Energy of the electron in first energy level,

$$E_1 = -\frac{1.312 \times 10^6}{1^2} \text{ J mol}^{-1} = -1.312 \times 10^6 \text{ J mol}^{-1}$$

Energy of the electron in third energy level,

$$E_3 = -\frac{1.312 \times 10^6}{3^2} \text{ J mol}^{-1} = -1.468 \times 10^5 \text{ J mol}^{-1}$$

Excitation energy $= E_3 - E_1 = -1.486 \times 10^5 \text{ J mol}^{-1} - (-13.12 \times 10^5 \text{ J mol}^{-1})$

$= \mathbf{+ 11.66 \times 10^5 \text{ J mol}^{-1}}$.

(*b*) Ionisation energy of hydrogen is the energy required to remove the electron from ground state (first energy level) to infinity. When electron is at infinitely large distance from the nucleus, its energy is assumed to be zero.

$\therefore$ Ionisation energy of hydrogen $= E_\infty - E_1$

$$= 0 - \left(-\frac{1.312 \times 10^6}{1^2} \text{ J mol}^{-1} \right) = \mathbf{1.312 \times 10^6 \text{ J mol}^{-1}}.$$

Example 1.18. (*a*) *What sub-shells are possible in n = 3 energy level ?*

(*b*) *How many orbitals (of all kinds) are possible in this level ?*

Solution. (*a*) *Sub-shells in n = 3 energy level.*

For $n = 3$, the possible values of l are 0, 1 and 2.

The corresponding sub-shells are

$l = 0$, *s* sub-shell
$l = 1$, *p* sub-shell
$l = 2$, *d* sub-shell

(*b*) *Number of orbitals*

For $n = 3$ there are one *s*, three *p* and five *d* orbitals.

This makes total of **nine orbitals** in $n = 3$ level.

Example 1.19. *Write the designations for orbitals with following quantum numbers :*

(*a*) $n = 3$, $l = 0$ (*b*) $n = 5$, $l = 2$.

Solution. (*a*) The designation for orbitals with $l = 0$ is *s*. Hence, the orbital with $n = 3$, $l = 0$ is **3*s***.

(*b*) The designation for orbitals with $l = 2$ is *d*. Hence the orbital with $n = 5$, $l = 2$ is **5*d***.

Example 1.20. *What are the possible values of l for an electron in (a) third energy level (b) 3d sub-shell.*

Solution. (*a*) For third energy level $n = 3$, since l may have values from 0 to $n - 1$, the possible values of l are **0, 1 and 2.**

(*b*) For *d*-sub-shell $l = 2$, hence, in 3*d*-sub-shell the only possible value of l is 2.

REVIEW PROBLEMS

1.32. Calculate the excitation energy required for the promotion of electron from the ground state of hydrogen to the fourth energy level.

1.33. How many orbitals are possible in

(*a*) 4th energy level (*b*) 5*f*-sub-shell ?

1.34. What are the possible values of *m* for the different orbitals of (*i*) *p*-sub-shell (*ii*) *d*-sub-shell.

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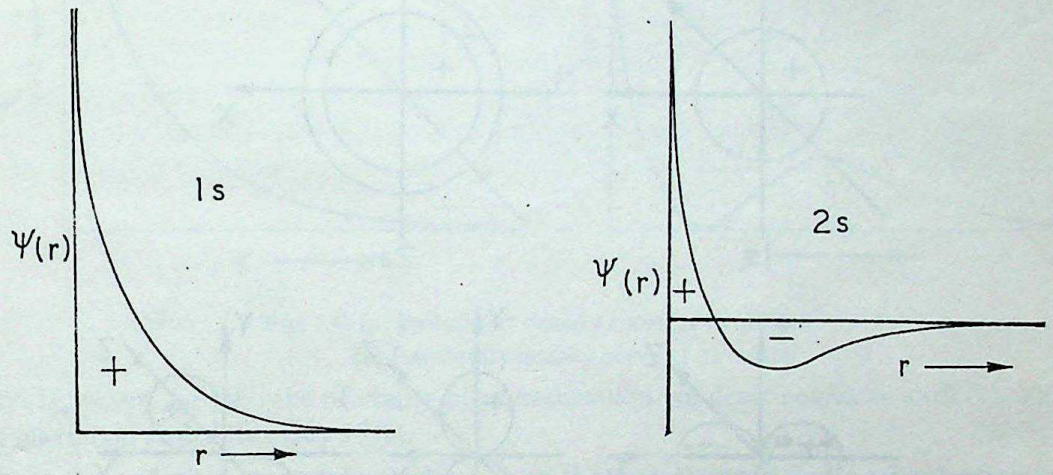
1.6. ORBITAL-WAVE FUNCTIONS, PROBABILITY DISTRIBUTION AND SHAPES OF ORBITALS

In order to understand the distribution of electrons in a given volume of space about the nucleus we need to know about the wave functions (*refer to section 1.4*). An orbital wave function (ψ) can be written as



(*a*) (*b*)

Fig. 1.6. (*a*) Variation of 1*s* orbital wave function with distance from the nucleus.
(*b*) Variation of 2*s* orbital wave function with distance from the nucleus.

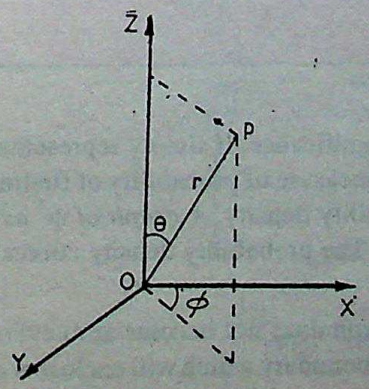
product of two functions, the **radial function** and the **angular function**. The radial function is function of distance only and the angular function is function of two angle variables

$$\psi = \psi(r) \cdot \psi(\theta, \phi)^*$$

Thus, the complete wave function represents an orbital in which the *radial part* $\psi(r)$ depends upon quantum numbers n and l and it tells us about the *size* of the orbital whereas the *angular part*, $\psi(\theta, \phi)$, depends upon quantum number l and m and tells us about the *shape* of the orbital. Because of the three variables involved, it is not easy to plot variation of ψ with these variables in a single diagram. In order to overcome this difficulty, the distance variation and the angular variation are plotted in separate diagrams. The variation of the radial part of the orbital wave function for 1*s* and 2*s* orbitals is given in Fig. 1.6.

Significance of plots. As ψ has no significance therefore the above plots are also meaningless except that the plots give the sign of wave function.

It has been observed that ***s*-orbitals** are independent of angular wave function, but simply depends on radial part of wave function. This means that they do not have directional dependence. All *s*-orbitals are,



*Here r, θ and ϕ are spherical polar co-ordinates. Since the Schrödinger wave equation has more utility in the form of spherical coordinates instead of cartesian coordinates, therefore, the location of a point p in shperical coordinate system relative to cartesian coordinates is shown in the figure.

r is the length of the line between origin and the point p. The angle between this line and the z-axis is θ. ϕ is the angle that projection of this line in the xy-plane makes with x-axis.

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therefore, **spherically symmetrical**. *p*- and *d*-orbitals however, depend upon radial as well as angular wave functions, which means they show angular dependence. The angular dependence of 1*s*, 2*s* and 2*p* orbital wave functions has been illustrated in Fig. 1.7.

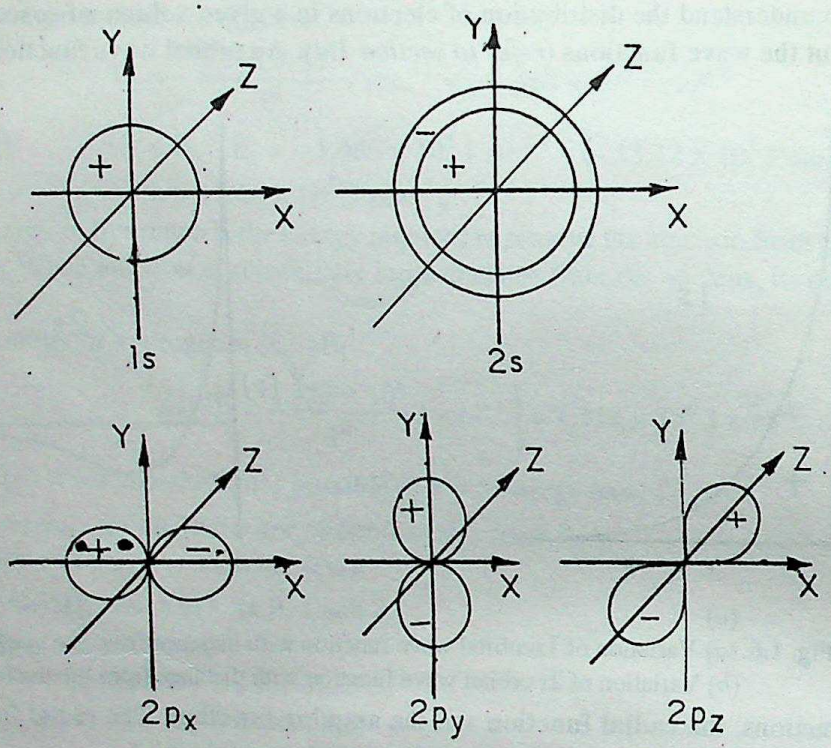

Fig. 1.7. Angular plots of 1*s*, 2*s* and 2*p* orbitals.

The positive and negative signs in Fig. 1.6 and Fig. 1.7 indicate whether the orbital wave function is positive or negative in a particular region. These signs do not represent the positive or negative charge. They are just analogous to the signs of amplitude in case of plane waves. It may be noted that 1*s* orbital wave function has same sign everywhere. This is equivalent to the wave produced by plucking the string between the two points in the middle as shown in Fig. 1.8 (*a*). On the other hand, 2*s* orbital wave function can be positive or negative depending upon the distance. In fact the sign of wave function changes after the node. This is equivalent to the wave produced when the string between the two points is plucked at $\frac{1}{4}$ th of a distance Fig. 1.8 (*b*).

Fig. 1.8

Probability Density $(\psi)^2$

The orbital wave function, ψ, as such has no physical significance. It simply represents amplitude of the electron wave. However, square of wave function, ψ^2, is the measure of probability of finding the electron in a unit volume around a particular point and is called probability density. *A graph of ψ^2 as a function of distance from the nucleus* is called **probability density curve.** The probability density curves for 1*s* and 2*s* orbitals are shown in Fig. 1.9.

It may be noted that the probability of finding the electron does not become zero even at very large distances from the nucleus. Therefore, it is not possible to draw a boundary which will enclose regions of 100%

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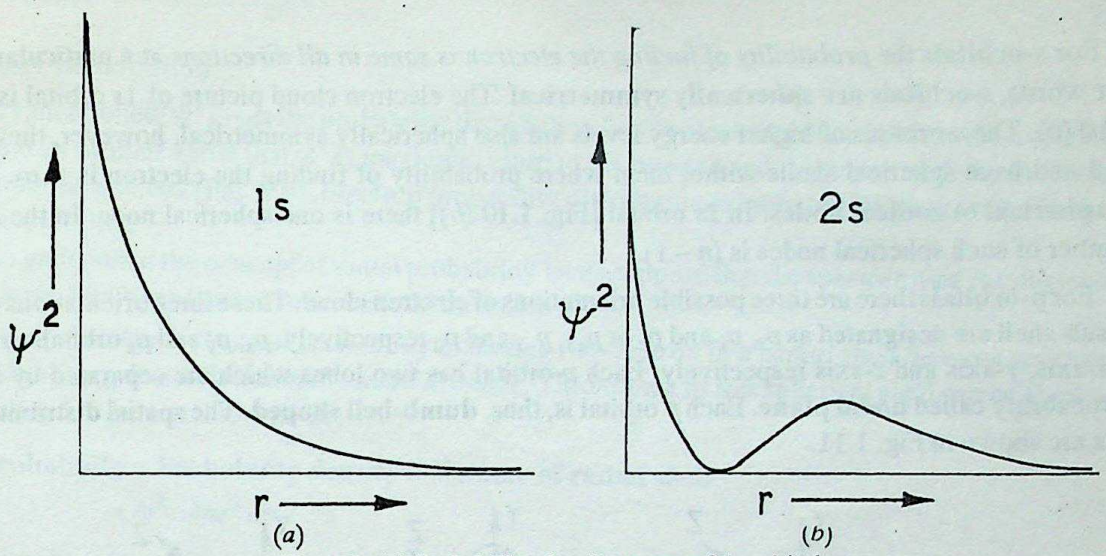

Fig. 1.9. (*a*) Probability density curve of 1*s* orbital.
(*b*) Probability density curve of 2*s* orbital.

probability. However, for the sake of clarity of representation we draw boundary surfaces which enclose regions of maximum probability (say 99%).

The regions of space around the nucleus where the probability of finding the electron is maximum are called orbitals.

The boundary surfaces of ψ^2 are quite similar to that of ψ (Fig. 1.7). However, there is one main qualitative **difference** that ψ may have negative sign in some regions whereas ψ^2 is always positive.

Charge Cloud Picture of Orbitals

An alternative way to describe the probability is in terms of negative charge cloud, the density of charge cloud being proportional to ψ^2 or probability. In this method, the charge cloud is represented in term of small dots. To understand, this method of representation let us imagine the electron as a very small dot. Let us further suppose that we take a very large number of photographs of the electron in a hydrogen atom at very short interval of time on the same film. If the film were developed, the picture obtained would be similar to that shown in Fig. 1.10 (*a*). In terms of electron cloud representation the probability of finding the electron in a particular region of space is directly proportional to the density of such dots in that region.

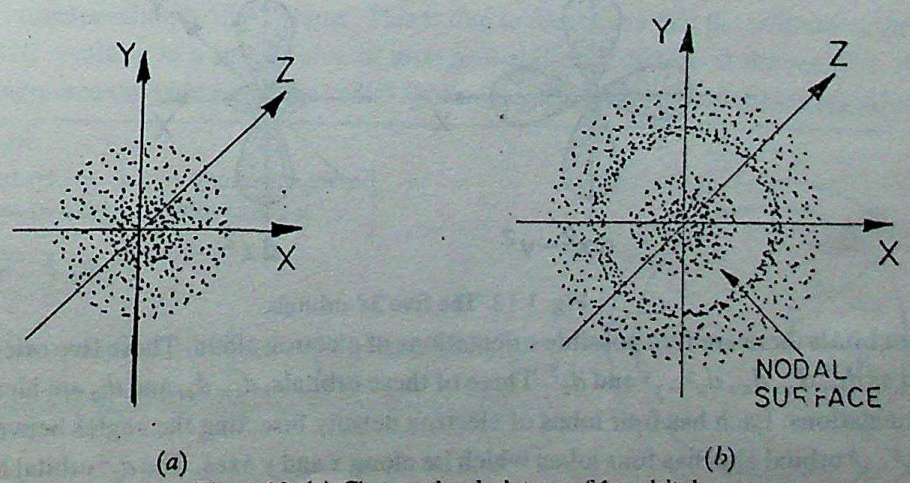

Fig. 1.10. (*a*) Charge cloud picture of 1*s* orbital
(*b*) Charge cloud picture of 2*s* orbital.

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For **s-orbitals** the *probability of finding the electron is same in all directions* at a particular distance. In other words, **s-orbitals are spherically symmetrical.** The electron cloud picture of 1*s* orbital is shown in Fig. 1.10 (*a*). The *s*-orbitals of higher energy levels are also spherically symmetrical, however, they are more diffused and have spherical shells within them where probability of finding the electron is zero. These are called **spherical** or **radical nodes.** In 2*s* orbital [Fig. 1.10 (*b*)] there is one spherical node. In the *ns* orbital, the number of such spherical nodes is $(n-1)$.

For **p-orbitals** there are three possible orientations of electron cloud. These three orientations or orbitals of a *p*-sub-shell are designated as p_x, p_y and p_z or p_{+1}, p_{-1} and p_0 respectively. p_x, p_y and p_z orbitals are oriented along *x*-axis, *y*-axis and *z*-axis respectively. Each *p*-orbital has two lobes which are separated by a plane of zero probability called **nodal plane.** Each *p* orbital is, thus, **dumb-bell shaped.** The spatial distributions of 2*p* orbitals are shown in Fig. 1.11.

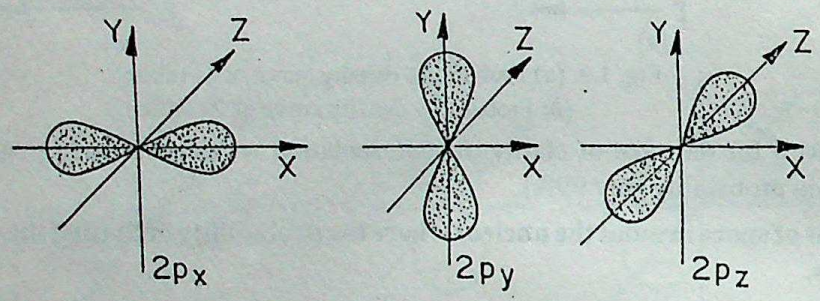

Fig. 1.11. 2*p* orbitals.

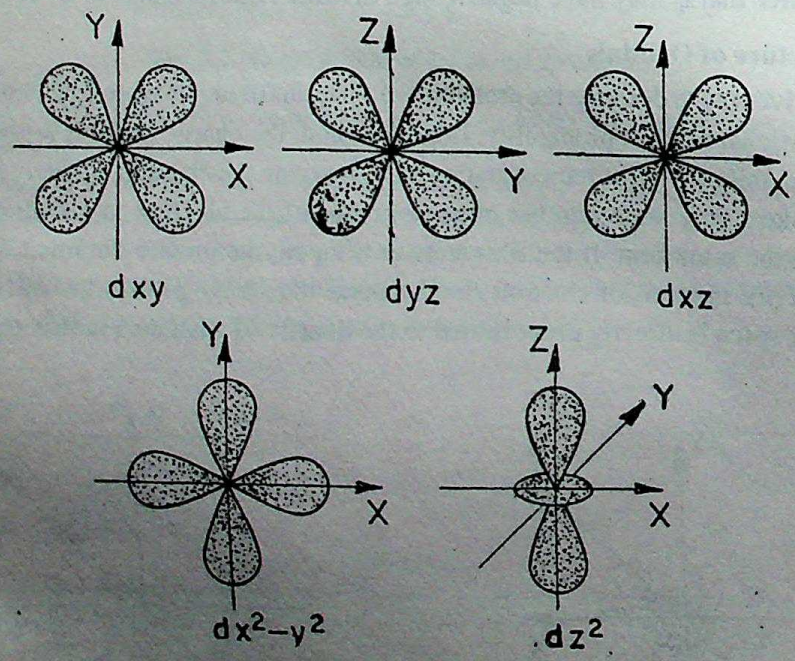

Fig. 1.12. The five 3*d*-orbitals.

For **d-orbitals** there are five possible orientations of electron cloud. These five orientations or orbitals are designated as d_{xy}, d_{yz}, d_{xz}, $d_{x^2-y^2}$ and d_{z^2}. Three of these orbitals, d_{xy}, d_{yz} and d_{xz} are identical in shape but different in orientations. Each has four lobes of electron density bisecting the angles between principal axes.

The $d_{x^2-y^2}$ orbital also has four lobes which lie along *x* and *y* axes. The d_{z^2} orbital has two lobes lying along *z*-axis and a ring of high electron density in the *xy* plane as shown in Fig. 1.12.

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Radial Probability Distribution

As already mentioned, ψ^2 gives the probability distribution for the electron with respect to the nucleus. The plots of 1*s* and 2*s* orbitals show that ψ^2 is maximum close to the nucleus and decreases with the increase in the distance from the nucleus (Fig. 1.9). Electron probability distribution is more usefully expressed in the form of **radial probability.**

In order to understand the concept of radial probability let us suppose that the space around the nucleus is divided into a large number of concentric shells of thickness *dr*.

The radial probability is the total probability of finding the electron in a radial shell between spheres of radii r and r + dr, where dr is infinitesimally small distance. The volume of this spherical shell can be shown by simple calculation* to be equal to $4\pi r^2 dr$.

Radial probability = Probability density × Volume of radial shell

$$= \psi^2 \cdot 4\pi r^2 dr.$$

From the above relation it is clear that radial probability not only depends upon probability density but also on the volume of the radial shell.

In Fig. 1.13, the probability density (ψ^2) for 1*s* orbital is plotted against distance from the nucleus. It is clear from the figure that the probability is greatest near the nucleus and it goes on decreasing with distance. The volume of the radial shell is also plotted at various distances from the nucleus (shown by dotted lines). The volume of shell goes on increasing with increase in distance.

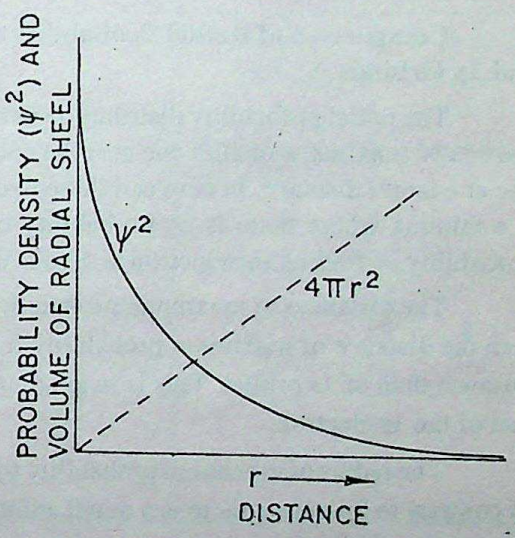


Fig. 1.13. Plot of ψ^2 and volume of shell versus *r* for 1*s* electron.

The product of probability density and volume of shell gives radial probability ($\psi^2 \cdot 4\pi r^2 dr$). The radial probability curves for 1*s*, 2*s* and 2*p* orbitals are given in Fig. 1.14.

If we observe the radial probability distribution curve of 1*s* orbital, we find that it is quite different from probability density graph (ψ^2 vs. *r*). The probability density (ψ^2) is maximum close to the nucleus but the total probability is least corresponding to this volume. This is due to the reason that the volume of the shell near the nucleus is very small resulting in a small value of total probability. It is zero at the nucleus. As the distance from the nucleus increases the volume of the radial shell increases while ψ^2 decreases rapidly. As a

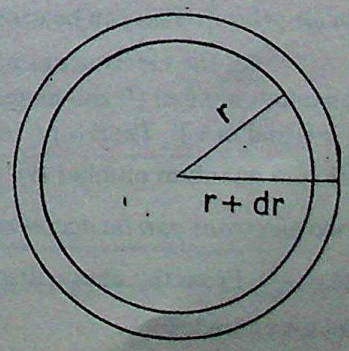
---

***Volume of radial shell**

$$= \begin{bmatrix} \text{Volume of sphere} \\ \text{with radius } (r + dr) \end{bmatrix} - \begin{bmatrix} \text{Volume of sphere} \\ \text{with radius } r \end{bmatrix}$$

$$= \frac{4}{3}\pi(r + dr)^3 - \frac{4}{3}\pi r^3$$

$$= \frac{4}{3}\pi(r^3 + 3r^2dr + 3rdr^2 + dr)^3 - \frac{4}{3}\pi r^3 = \frac{4}{3}\pi[r^3 + 3r^2dr - r^3]$$



(As *dr* represents an extremely small thickness, the higher powers of *dr* such as dr^2 and dr^3 may be neglected.)

$$\therefore \quad \text{Volume of shell} = \frac{4}{3}\pi \times 3r^2dr = 4\pi r^2 dr.$$

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result of this, the probability keeps on increasing gradually and reaches a maximum value and then decreases gradually. The maximum in the curve indicates the most probable value and the corresponding distance from the nucleus is called **distance of maximum probability** (r_0). For hydrogen atom, this radius has a value of 53 *pm*.

It is important to note that Bohr predicted that the electron will always be at r = 53 pm for hydrogen atom. However, according to wave mechanical model the electron is most likely to be found at this distance and there is probability of finding the electron at distances both shorter and larger than 53 pm.

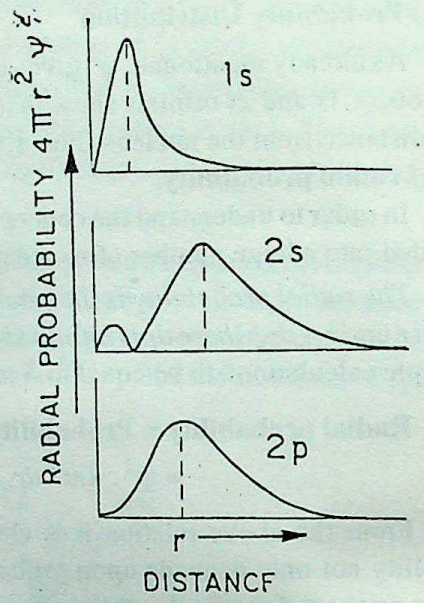

Fig. 1.14. Radial probability distribution curves for 1*s*, 2*s* and 2*p*-orbitals.

Comparison of Radial Probability curves of 1s, 2s and 2p Orbitals.

The radial probability distribution curve for 2*s* orbital shows two maxima, a smaller one near the nucleus and bigger one at a larger distance. In between these two maxima, there is a minima where there is no probability of finding the electron at that distance. The point at which the probability of finding the electron is zero is called a **nodal point.**

The distances of maximum probability for 2*s* and 2*p* orbitals are approximately the same but are larger than the distance of maximum probability for 1*s* orbital. This means that 2*s* and 2*p* electrons are at a greater distance than of 1*s* orbital. This is in keeping with the fact that 2*s* and 2*p* electrons have greater energy than that of the 1*s* electron.

The radius of maximum probability for a 2*p* electron is slightly less than that for a 2*s* electron. However, in contrast to 2*p* curve, there is a small additional maxima in the 2*s* curve. This indicates that the electron in 2*s* orbital spends some of its time near the nucleus. In other words, 2*s* electron penetrates a little closer to the nucleus, and is, therefore, held more tightly than the 2*p* electron.

Thus, 2*s* electron is more stable and has lower energy than a 2*p* electron.

1.7. PAULI'S EXCLUSION PRINCIPLE

This principle was discovered by Wolfgang Pauli in 1925. Pauli's exclusion principle states that :

No two electrons in an atom can have same values for all the four quantum numbers.

A direct implication of this principle is that *it is not possible to accommodate more than two electrons in an orbital.* This can be easily understood as follows :

All the electrons in particular orbital have same values of principal quantum number (n), azimuthal quantum number (l) and magnetic quantum number (m). For example, all the electrons in 3*s* orbital have $n = 3$, $l = 0$ and $m = 0$. Therefore, in order to have unique sets of quantum numbers they must have different values of spin quantum number (s). But we know s can have only two values $+\frac{1}{2}$ and $-\frac{1}{2}$. Hence, *in an orbital only two electrons can be accommodated, one spinning clockwise* ($s = +\frac{1}{2}$) *and the other spinning anti-clockwise* ($s = -\frac{1}{2}$). From the above discussion we can derive the number of electrons in different types of sub-shells as given under :

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Type of sub-shell	*Number of orbitals*	*Number of Electrons*
s-sub-shell	1	1 × 2 = 2
p-sub-shell	3	3 × 2 = 6
d-sub-shell	5	5 × 2 = 10
f-sub-shell	7	7 × 2 = 14

On the basis of this principle it is possible to calculate the number of electrons in various energy levels as given in Table 1.3.

Table 1.3. Distribution of Electrons in Different Energy Levels and their Quantum Numbers

Principal Energy Level	*Possible values of diffrerent quantum numbers*				*Sub-shell designation*	*Total number of electrons*	
	n	*l*	*m*	*s*		*In the sub-shell*	*In the energy level*
K	1	0	0	+ ½, − ½	1*s*	2	2
L	2	0	0	+ ½, − ½	2*s*	2	8
		1	+1	+ ½, − ½	2*p*	6	
			0	+ ½, − ½			
			−1	+ ½, − ½			
M	3	0	0	+ ½, − ½	3*s*	2	18
		1	+1	+ ½, − ½	3*p*	6	
			0	+ ½, − ½			
			−1	+ ½, − ½			
		2	+2	+ ½, − ½	3*d*	10	
			+1	+ ½, − ½			
			0	+ ½, − ½			
			−1	+ ½, − ½			
			−1	+ ½, − ½			

1.8. ENERGY LEVEL DIAGRAMS

A diagram representing relative energies of various orbitals in an atom is called energy level diagram.

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Energy Level Diagram of Hydrogen Atom

In hydrogen atom there is only one electron which is present in 1*s* orbital in ground state. However, in excited state the electron may jump to any of the orbitals belonging to higher energy levels.

Energies of the higher energy levels for hydrogen atom and hydrogen-like species is given by the expression,

$$E_n = -k^2 \frac{2\pi^2 me^4 Z^2}{n^2 h^2} \quad ...(i)$$

$$= -\frac{2.178 \times 10^{-18}}{n^2} . Z^2 \text{ J/atom} = -\frac{1312}{n^2} . Z^2 \text{ kJ/mole}$$

The k in relation (*i*) is a constant and its value is 9.0×10^9 J.m/C^2. k is inverse of permittivity factor.

For H atom nuclear charge, Z = 1

whereas for hydrogen-like species, such as He^+, Li^{2+}, Be^{+3}, Z is equal to 2, 3, 4 respectively.

The energies of various orbitals belonging to these energy levels can also be calculated.

The relative energies of these orbitals have been represented in Fig. 1.14 (*a*).

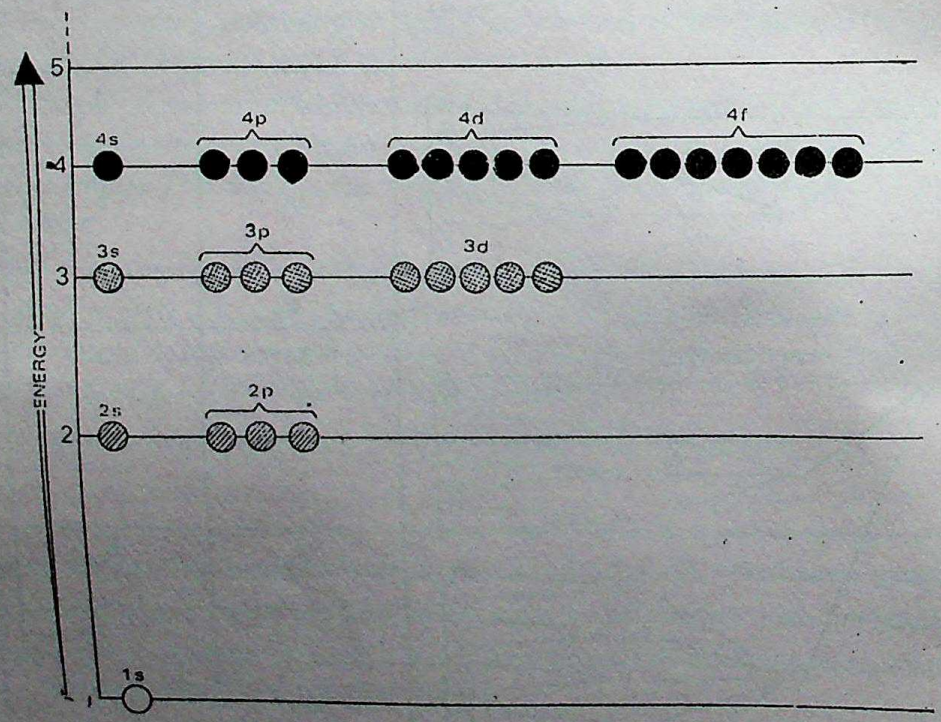

Fig. 1.14. (*a*) Energy level diagram of hydrogen atom.

It may be noted that all the orbitals of a particular energy level have same energy in hydrogen and hydrogen-like species. For example, 2*s* and 2*p* orbitals have same energy. *It is so because for an atom having a single electron, the principal quantum number, n is most important in determining the energy of the orbital. The value of l* (the angular momentum quantum number) *merely determines the shape of the orbital.*

Energy Level Diagram of Multi-electron Atoms

In case of multi-electron atoms the energies of various orbitals depend not only upon the nuclear charge but also upon the other electrons present in the atom. It is impossible to calculate the exact energies of various

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orbitals in a multi-electron atom. However, approximate values of their energies can be obtained from the spectral data. Relative order of energies of various orbitals in all multi-electron atoms is same and is illustrated in Fig. 1.15. Main characteristics of this diagram are :

(*i*) The different sub-shells of a particular energy level may have different energies. For example, energy of 2*s* sub-shell is different from the energy of 2*p* sub-shell.

(*ii*) In a particular energy level, the sub-shell having higher value of *l* has higher energy. For example, energy of 2*p* sub-shell ($l = 1$) is higher than energy of 2*s* sub-shell ($l = 0$). In general, increasing order of energies of different types of sub-shells in a particular energy level is

$$s < p < d < f.$$

(*iii*) As the value of *n* increase, some sub-shell of lower energy level may have energy higher than the energy of some sub-shell of higher energy level. For example, energy of 3*d* is higher than the energy of 4*s* although the latter belongs to higher main energy level.

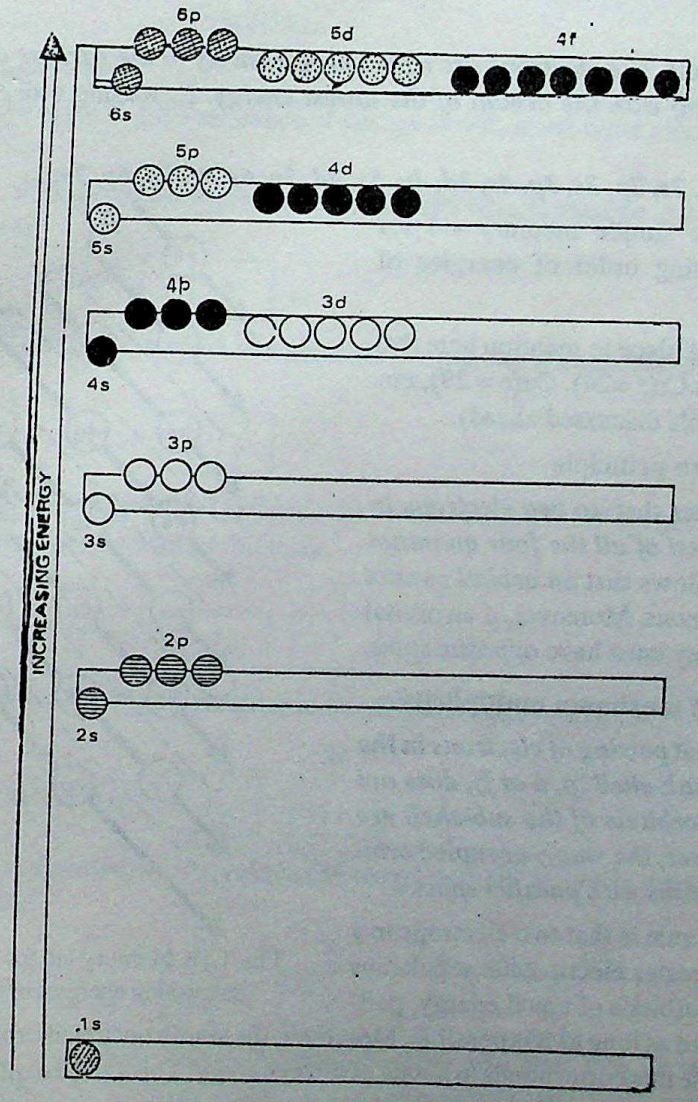

Fig. 1.15. Energy level diagram of multi-electron atoms.

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(*iv*) The increasing order of energies of various sub-shells is

$$1s < 2s < 2p < 3s < 3p < 4s < 3d < 4p < 5s < 4d < 5p.....$$

In a multi-electron atom energy of electron is determined not only by principal quantum number (n) but also by azimuthal quantum number (l). The relative order of energies of various sub-shells in a multi-electron atom can be predicted with the help of **(n + l) rule** or **Bohr-Bury's rule**. According to this rule :

(*a*) *In neutral atoms a sub-shell with lower value of (n + l) has lower energy.*

(*b*) *If two sub-shells have equal value of (n + l), the sub-shell with lower value of n has lower energy.*

1.9. RULES FOR FILLING OF ORBITALS IN AN ATOM

An atom in its lowest energy state is said to be in the normal state or the *ground state*. The ground state is the most stable state for the atom. The filling of orbitals in the ground state is determined by the following *rules* :

1. Aufbau rule

According to this rule, ***the electrons are added progressively to the various orbitals in the order of increasing energies starting with the orbital of the lowest energy***. Increasing order of energies of various orbitals is :

1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s, 4d, 5p, 6s, 4f, 5d, 6p, 7s.....

Fig. 1.16 shows a simple memory aid for remembering the increasing order of energies of various sub-shells.

It may not be out of place to mention here that certain configurations like Cr(z =24), Cu(z = 29), etc. do not obey this rule (details discussed ahead).

2. Pauli's exclusion principle

This principle states that ***no two electrons in an atom can have same set of all the four quantum numbers***. From this it follows that ***an orbital cannot have more than two electrons***. Moreover, if an orbital has two electrons then they must have *opposite spins*.

3. Hund's rule of maximum multiplicity

This rule states that ***pairing of electrons in the orbitals of a particular sub-shell (p, d or f), does not take place until all the orbitals of the sub-shell are singly occupied. Moreover, the singly occupied orbitals must have the electrons with parallel spins.***

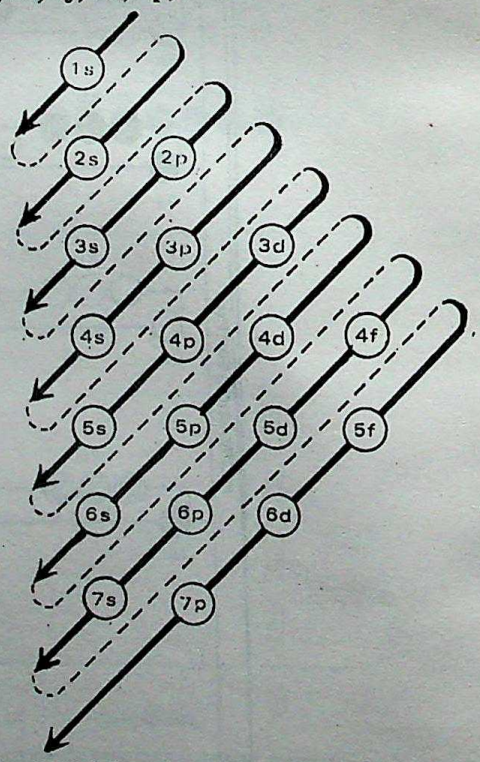

Fig. 1.16. Memory aid for remembering order of increasing energies of various sub-shells.

The basis of this rule is that two electrons in a particular orbital feel greater electrostatic repulsions and hence while filling orbitals of equal energy, pairing of electrons is avoided as long as it is possible. Moreover, the singly occupied orbitals should have electrons with parallel spin because this corresponds to a state of lower energy. This can be explained in terms of magnetic effects of electron spin. Hund's rule helps us in writing the ground state configurations of those atoms which have partially filled *p*, *d* or *f* sub-shells in them.

The application of these rules has been illustrated in the electronic configurations on page 35.

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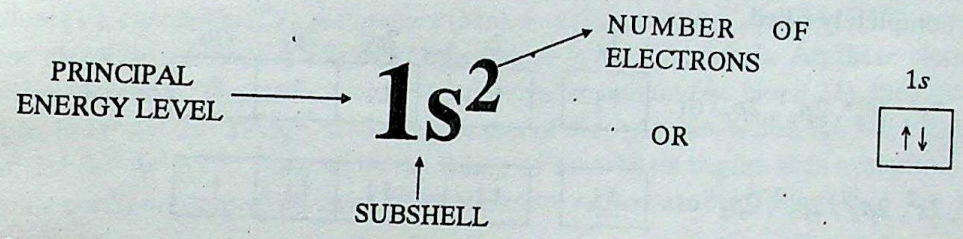
1.10. REPRESENTATION OF ELECTRONIC CONFIGURATIONS

In order to represent electron population of an orbital, the principal quantum number (n) is written before the orbital symbol while the number of electrons in the orbital is written as superscript near the right hand top of the orbital symbol. For example, if we have two electrons in the s-orbital of first energy level then it is written as $1s^2$. Sometimes, electronic configurations are represented in a different manner by representing each orbital by a square or a circle and the electrons are representing by putting arrows in it as illustrated below :



Electronic Configuration of Atoms

On the basis of above rules and the sequence of energy levels, let us write electronic configurations of some elements.

Hydrogen (At. No. = 1). Since hydrogen has only one electron, it must go to $1s$ orbital. The electronic configuration for hydrogen is

$_1$**H :** $1s^1$ or [↑]

Helium (At. No. = 2). In helium atom, the second electron can also go into $1s$ orbital. The electrons must have opposite spins.

$_2$**He :** $1s^2$ or [↑↓]

Lithium (At. No. = 3). Since $1s$ orbital is filled with two electrons, it cannot have any more. Therefore, third electron goes to the next lowest energy orbital, $2s$.

$_3$**Li :** $1s^2, 2s^1$ or [↑↓] [↑] (1s, 2s)

Beryllium (At. No. = 4). The fourth electron in beryllium fills $2s$ orbital.

$_4$**Be :** $1s^2, 2s^2$ or [↑↓] [↑↓] (1s, 2s)

Boron (At. No. = 5). In this case, the four electrons completely fill $1s$ and $2s$ orbitals. The fifth electron goes into one of the $2p$ orbitals.

$_5$**B :** $1s^2, 2s^2, 2p_x^1$ or [↑↓] [↑↓] [↑] [ ] [ ] (1s, 2s, $2p_x$, $2p_y$, $2p_z$)

Carbon (At. No. = 6). In case of carbon the sixth electron also goes into $2p$ sub-shell, but the two electrons in $2p$ subs-shell are present in different orbitals because according to Hund's rule pairing of electrons cannot take place in orbitals of a particular sub-shell until all the orbitals get one electron each. Hence, configuration of carbon is

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		1s	2s	$2p_x$	$2p_y$	$2p_z$
$_6C$:	$1s^2, 2s^2, 2p_x^1, 2p_y^1$ or	↑↓	↑↓	↑	↑	

Nitrogen (At. No. = 7). Applying Hund's rule, N atom has three unpaired electrons in $2p$ orbitals.

		1s	2s	$2p_x$	$2p_y$	$2p_z$
$_7N$:	$1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ or	↑↓	↑↓	↑	↑	↑

Oxygen flourine and neon. Beginning with oxygen, the $2p$ orbitals start filling by second electron till neon in which it is completely filled.

		1s	2s	$2p_x$	$2p_y$	$2p_z$
$_8O$:	$1s^2, 2s^2, 2p_x^2, 2p_y^1, 2p_z^1$ or	↑↓	↑↓	↑↓	↑	↑
$_9F$:	$1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^1$ or	↑↓	↑↓	↑↓	↑↓	↑
$_{10}Ne$:	$1s^2, 2s^2, 2p_x^2, 2p_y^2, 2p_z^2$ or	↑↓	↑↓	↑↓	↑↓	↑↓

From sodium (At. No. 11) to Argon (At. No. 18) $3s$ and $3p$ orbitals are successively filled. After $3p$ the 19th electron in potassium (At. No. 19) enters the $4s$ orbital instead of $3d$ because energy of $4s$ orbitals is less than that of $3d$. Electronic configurations of first twenty elements have been given in Table 1.4.

Table 1.4. Electronic Configurations of the First 20 Elements

At. No.	*Element*	*Orbital Electronic Configuration*			
1.	Hydrogen	$1s^1$			
2.	Helium	$1s^2$			
3.	Lithium	$1s^2$	$2s^1$		
4.	Beryllium	$1s^2$	$2s^2$		
5.	Boron	$1s^2$	$2s^2 2p_x^1$		
6.	Carbon	$1s^2$	$2s^2 2p_x^1 2p_y^1$		
7.	Nitrogen	$1s^2$	$2s^2 2p_x^1 2p_y^1 2p_z^1$		
8.	Oxygen	$1s^2$	$2s^2 2p_x^2 2p_y^1 2p_z^1$		
9.	Flourine	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^1$		
10.	Neon	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$		
11.	Sodium	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^1$	
12.	Magnesium	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2$	
13.	Aluminium	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^1$	
14.	Silicon	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^1 3p_y^1$	
15.	Phosphorus	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^1 3p_y^1 3p_z^1$	
16.	Sulphur	$1s^2$	$2s^2 2p_x^2 2p_y^2 2p_z^2$	$3s^2 3p_x^2 3p_y^1 3p_z^1$	

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At. No.	Element		Orbital Electronic Configuration		
17.	Chlorine	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$.	$3s^2\,3p_x^2\,3p_y^2\,3p_z^1$	
18.	Argon	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$.	$3s^2\,3p_x^2\,3p_y^2\,3p_z^2$	
19.	Potassium	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,3p_x^2\,3p_y^2\,3p_z^2$	$4s^1$
20.	Calcium	$1s^2$	$2s^2\,2p_x^2\,2p_y^2\,2p_z^2$	$3s^2\,3p_x^2\,3p_y^2\,3p_z^2$	$4s^2$

The next ten *elements* (At. Nos. = 21—30) which follow calcium are *scandium* (Sc), *titanium* (Ti), *vanadium* (V), *chromium* (Cr), *manganese* (Mn), *iron* (Fe), *cobalt* (Co), *nickel* (Ni), *copper* (Cu) and *zinc* (Zn). In these elements *addition of electrons takes place in the 3d-orbitals.* All these elements are known as the **transition elements.** The electronic configuration of scandium (At. No. = 21), the first transition element, for example, is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^1$ while that of zinc (At. No. = 30), the last element of the series, is $1s^2\,2s^2\,2p^6\,3s^2\,3p^6\,4s^2\,3d^{10}$. Thus, while the filling of 3*d*-orbitals begins with scandium, it ends with zinc. The electronic configurations of all these 10 elements are represented in Table 1.5.

Table 1.5. Electronic Configurations of Transition Elements

[Scandium (At. No. 21) to Zinc (At. No. 30)]

Atomic Number	Element	Electronic Configuration			
21	Scandium	$1s^2$	$2s^2\,2p^6$	$3s^2\,3p^6\,3d^1$	$4s^2$
22	Titanium	$1s^2$	$2s^2\,2p^6$	$3s^2\,3p^6\,3d^2$	$4s^2$
23	Vanadium	$1s^2$	$2s^2\,2p^6$	$3s^2\,3p^6\,3d^3$	$4s^2$
24	**Chromium**	$\mathbf{1s^2}$	$\mathbf{2s^2\,2p^6}$	$\mathbf{3s^2\,3p^6\,3d^5}$	$\mathbf{4s^1}$
25	Manganese	$1s^2$	$2s^2\,2p^6$	$3s^2\,3p^6\,3d^5$	$4s^2$
26	Iron	$1s^2$	$2s^2\,2p^6$	$3s^2\,3p^6\,3d^6$	$4s^2$
27	Cobalt	$1s^2$	$2s^2\,2p^6$	$3s^2\,3p^6\,3d^7$	$4s^2$
28	Nickel	$1s^2$	$2s^2\,2p^6$	$3s^2\,3p^6\,3d^8$	$4s^2$
29	**Copper**	$\mathbf{1s^2}$	$\mathbf{2s^2\,2p^6}$	$\mathbf{3s^2\,3p^6\,3d^{10}}$	$\mathbf{4s^1}$
30	Zinc	$1s^2$	$2s^2\,2p^6$	$3s^2\,3p^6\,3d^{10}$	$4s^2$

Exceptional Configurations of Chromium and Copper

From the above configurations (Table 1.5) it may be noted that chromium and copper have five and ten electrons in 3*d* orbitals rather than four and nine electrons respectively as expected. The reason is that ***fully-filled orbitals*** and ***exactly half-filled orbitals have extra stability***. (Thus, the p^3, p^6, d^5, d^{10}, f^7 and f^{14} configurations which are either fully-filled or exactly half-filled, are more stable). Therefore, to acquire more stability one of the 4*s* electron goes into 3*d* orbitals so that 3*d* orbitals get half-filled or completely filled in chromium and copper respectively.

The half-filled and completely filled degenerate orbitals provide extra stability to the system due to *symmetrical arrangement* and *exchange energy* as described below :

(*i*) ***Symmetrical arrangement.*** The electronic configurations in which all the orbitals of same sub-shell are either completely-filled or exactly half-filled have relatively more symmetrical distribution of electrons and therefore, lend more stability to the system. For example, expected configuration of chromium is $3d^4\,4s^2$. But shifting of one electron from 4*s* to 3*d*-orbitals makes the configuration more symmetrical and hence relatively more stable.

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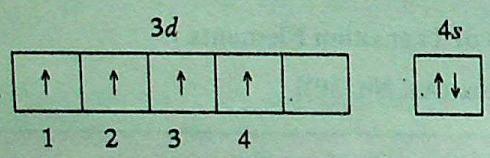
(Less symmetrical) (More symmetrical)

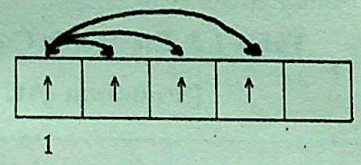
In the similar way shifting of one electron from 4*s* to 3*d* in copper also makes the configuration relatively more stable.

(Less symmetrical) (More symmetrical)

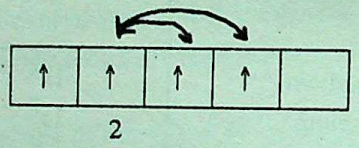
(*ii*) ***Stability due to exchange energy.*** The half-filled or fully-filled degenerate orbitals have more number of exchanges and consequently, have large exchange energy of stabilisation. The exchange mean shifting of electrons from one orbital to another with same sub-shell. Let us compare the number of exchanges in $3d^4\ 4s^2$ and $3d^5\ 4s^1$ configurations of chromium.



($3d^4$ configuration)

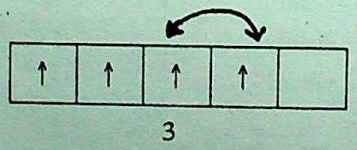


3 exchanges for electron 1



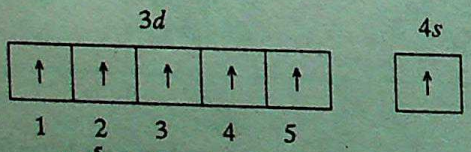
2 exchanges for electron 2

Total exchanges = 3 + 2 + 1 = 6



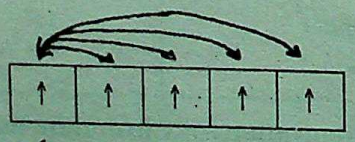
1 exchange for electron 3

Thus, in $3d^4$ arrangement electron exchanges are six which implies that there are six possible arrangements with parallel spin in $3d^4$ configuration.

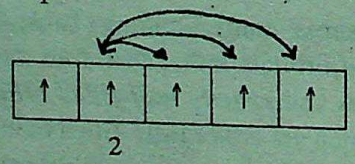


($3d^5$ configuration)

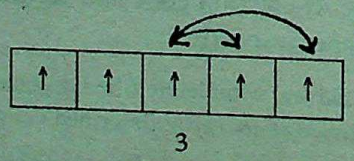
Total exchanges = 4 + 3 + 2 + 1 = 10



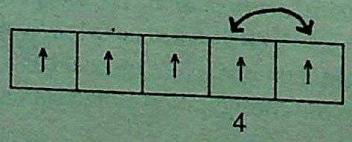
4 exchanges for electron 1



3 exchanges for electron 2



2 exchanges for electron 3



1 exchange for electron 4

It is quite evident from the above description that total number of electron exchanges in $3d^5$ arrangement is larger which lends it relatively greater stability. In the similar way it can be established that number of exchanges in $3d^{10}$ configuration is larger than in $3d^9$ configuration which makes $3d^{10}$ configuration relatively more stable.

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Writing the Configuration in Condensed Form

It may be noted that configurations of atoms can also be written in condensed form by taking the configurations of noble gases as core. The configurations of inert gases representing core are written as $[He]^2$, $[Ne]^{10}$, $[Ar]^{18}$, $[Kr]^{36}$, $[Xe]^{54}$ and $[Rn]^{86}$. For example, electronic configuration of scandium having atomic number 21 may be written as $_{21}Sc$: $[Ar]^{18}\ 3d^1\ 4s^2$.

The electronic configurations of other elements on this pattern have been given in Table 1.6.

Table 1.6. Electronic Configurations of Elements

Atomic Number	*Element*	*Electronic configuration*	*Atomic Number*	*Element*	*Electronic configuration*
1	H	$1s^1$	*41	Nb	$-4d^4\ 5s^1$
2	He	$1s^2$	*42	Mo	$-4d^5\ 5s^1$
3	Li	$[He]\ 2s^1$	43	Tc	$-4d^5\ 5s^2$
4	Be	$-2s^2$	*44	Ru	$-4d^7\ 5s^1$
5	B	$-2s^2\ 2p^1$	*45	Rh	$-4d^8\ 5s^1$
6	C	$-2s^2\ 2p^2$	*46	Pd	$-4d^{10}\ 5s^0$
7	N	$-2s^2\ 2p^3$	*47	Ag	$-4d^{10}\ 5s^1$
8	O	$-2s^2\ 2p^4$	48	Cd	$-4d^{10}\ 5s^2$
9	F	$-2s^2\ 2p^5$	49	In	$-4d^{10}\ 5s^2\ 5p^1$
10	Ne	$-2s^2\ 2p^6$	50	Sn	$-4d^{10}\ 5s^2\ 5p^2$
11	Na	$[Ne]\ 3s^1$	51	Sb	$-4d^{10}\ 5s^2\ 5p^3$
12	Mg	$-3s^2$	52	Te	$-4d^{10}\ 5s^2\ 5p^4$
13	Al	$-3s^2\ 3p^1$	53	I	$-4d^{10}\ 5s^2\ 5p^5$
14	Si	$-3s^2\ 3p^2$	54	Xe	$-4d^{10}\ 5s^2\ 5p^6$
15	P	$-3s^2\ 3p^3$	55	Cs	$[Xe]\ 6s^1$
16	S	$-3s^2\ 3p^4$	56	Ba	$-6s^2$
17	Cl	$-3s^2\ 3p^5$	57	La	$-5d^1\ 6s^2$
18	Ar	$-3s^2\ 3p^6$	58	Ce	$-4f^1\ 6s^2$
19	K	$[Ar]\ 4s^1$	59	Pr	$-4f^3\ 6s^2$
20	Ca	$-4s^2$	60	Nd	$-4f^4\ 6s^2$
21	Sc	$-3d^1\ 4s^2$	61	Pm	$-4f^5\ 6s^2$
22	Ti	$-3d^2\ 4s^2$	62	Sm	$-4f^6\ 6s^2$
23	V	$-3d^3\ 4s^2$	63	Eu	$-4f^7\ 6s^2$
24	Cr	$-3d^5\ 4s^1$	64	Gd	$-4f^7\ 5d^1\ 6s^2$
25	Mn	$-3d^5\ 4s^2$	65	Tb	$-4f^9\ 6s^2$
26	Fe	$-3d^6\ 4s^2$	66	Dy	$-4f^{10}\ 6s^2$
27	Co	$-3d^7\ 4s^2$	67	Ho	$-4f^{11}\ 6s^2$
28	Ni	$-3d^8\ 4s^2$	68	Er	$-4f^{12}\ 6s^2$
29	Cu	$-3d^{10}\ 4s^1$	69	Tm	$-4f^{13}\ 6s^2$
30	Zn	$-3d^{10}\ 4s^2$	70	Yb	$-4f^{14}\ 6s^2$
31	Ga	$-3d^{10}\ 4s^2\ 4p^1$	71	Lu	$-4f^{14}\ 5d^1\ 6s^2$
32	Ge	$-3d^{10}\ 4s^2\ 4p^2$	72	Hf	$-4f^{14}\ 5d^2\ 6s^2$
33	As	$-3d^{10}\ 4s^2\ 4p^3$	73	Ta	$-4f^{14}\ 5d^3\ 6s^2$
34	Se	$-3d^{10}\ 4s^2\ 4p^4$	74	W	$-4f^{14}\ 5d^4\ 6s^2$
35	Br	$-3d^{10}\ 4s^2\ 4p^5$	75	Re	$-4f^{14}\ 5d^5\ 6s^2$
36	Kr	$-3d^{10}\ 4s^2\ 4p^6$	76	Os	$-4f^{14}\ 5d^6\ 6s^2$
37	Rb	$[Kr]\ 5s^1$	77	Ir	$-4f^{14}\ 5d^7\ 6s^2$
38	Sr	$-5s^2$	*78	Pt	$-4f^{14}\ 5d^9\ 6s^1$
39	Y	$-4d^1\ 5s^2$	*79	Au	$-4f^{14}\ 5d^{10}\ 6s^1$
40	Zr	$-4d^2\ 5s^2$	80	Hg	$-4f^{14}\ 5d^{10}\ 6s^2$

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Atomic Number	Element	Electronic configuration	Atomic Number	Element	Electronic configuration
81	Tl	$-4f^{14}\,5d^{10}\,6s^2\,6p^1$	93	Np	$-5f^4\,6d^1\,7s^2$
82	Pb	$-4f^{14}\,5d^{10}\,6s^2\,6p^2$	94	Pu	$-5f^6\,7s^2$
83	Bi	$-4f^{14}\,5d^{10}\,6s^2\,6p^3$	95	Am	$-5f^7\,7s^2$
84	Po	$-4f^{14}\,5d^{10}\,6s^2\,6p^4$	96	Cm	$-5f^7\,6d^1\,7s^2$
85	At	$-4f^{14}\,5d^{10}\,6s^2\,6p^5$	97	Bk	$-5f^9\,7s^2$
86	Rn	$-4f^{14}\,5d^{10}\,6s^2\,6p^6$	98	Cf	$-5f^{10}\,7s^2$
87	Fr	$[Rn]\,7s^1$	99	Es	$-5f^{11}\,7s^2$
88	Ra	$-7s^2$	100	Fm	$-5f^{12}\,7s^2$
89	Ac	$-6d^1\,7s^2$	101	Md	$-5f^{13}\,7s^2$
90	Th	$-6d^2\,7s^2$	102	No	$-5f^{14}\,7s^2$
91	Pa	$-5f^2\,6d^1\,7s^2$	103	Lr	$-5f^{14}\,6d^1\,7s^2$
92	U	$-5f^3\,6d^1\,7s^2$			

CHEMICAL BONDING

A chemical bond, *in general, may be defined as the force of attraction that binds the constituent particles (i.e., atoms or molecules or ions) together in various chemical species.* In the pervious class, we have already learnt that the atoms enter into chemical combination to form molecules because by doing so they attain the state of lowest energy or maximum stability. Based on this basic idea the formation of a number of different kinds of bonds like ionic, covalent, hydrogen and some others have already been discussed in the previous class.

The concept of covalent bond formation based on sharing of electrons (*Lewis concept*), as already discussed, was a purely qualitative approach. The above basis could not offer a satisfactory answer regarding the forces of attractive interactions in a molecule. In order to offer a reasonable explanation the modern researchers, based on wave mechanics, proposed two theories which are :

(*i*) *Valence Bond Theory (VBT)*

(*ii*) *Molecular Orbital Theory (MOT).*

1.11. REVIEW OF VALENCE BOND THEORY

In the previous class, we studied the formation of covalent bond in molecules in terms of **Valence Bond Theory**. This approach was put forward by Heitler and London in 1927 and was later developed by Linus Pauling and emphasizes on the participation of the valence electrons in the chemical bond formation. **Salient features** of this theory are summed up below :

(*i*) *According to this theory atoms maintain their individuality even in the molecule and the bond is formed by the interaction of half-filled orbitals belonging to the valence shells of the participating atoms.*

(*ii*) *The overlapping atomic orbitals must contain the electrons with opposite spins.*

(*iii*) *The strength of the bond depends upon the extent of overlapping. The greater the overlap stronger is the bond.*

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(iv) *As a result of overlapping and therefore pairing of electrons energy is released and hence the system acquires a state of lower energy.*

(v) *The stability of the molecule is further explained in terms of the exchange of electrons between the atoms participating in bond formation.*

(vi) *The valency of an element is equal to the number of half- filled orbitals in the valence shell of its atoms.*

The theory successfully explained the formation of hydrogen molecule. Besides this, the application of these ideas was also extended to molecules like F_2, NH_3, H_2O, CH_4, C_2H_2, etc. Though the theory could quite reasonably explain the shapes and bonding of many molecules, yet it failed to explain the magnetic properties of some of the molecules. For example, it could not explain why oxygen is paramagnetic in behaviour. Besides this, the theory fails to explain the bonding in electron deficient compounds as well as metals and intermetallic compounds.

The second approach, Molecular Orbital Theory, which though somewhat complicated, can explain the bonding in covalent molecules more satisfactorily.

1.12. MOLECULAR ORBITAL THEORY

Molecular orbital theory was put forward by Hund and Mulliken in 1932. The theory is modern and more rational. It assumes that in molecules atomic orbitals lose their indentity and the electrons in molecules are present in new orbitals called molecular orbitals which are not associated with a particular atom but belong to the molecule as a whole.

The **salient features** of this theory are given below :

(i) *In molecules, electrons are present in new orbitals called* **molecular orbitals.** *Molecular orbitals like atomic orbitals are characterized by a set of quantum numbers.*

(ii) *Molecular orbitals are formed by combination of atomic orbitals of nearly same energies.*

(iii) *Molecular orbitals are not associated with a particular atom but belong to nuclei of all the atoms constituting molecule. Nuclei of different atoms in the molecule behave as a polycentric nucleus.*

(iv) *The number of molecular orbitals formed is equal to the number of atomic orbitals undergoing combination. Among the new molecular orbitals formed, half are of lower energy than combining atomic orbitals* **(bonding orbitals)** *and the other half are of energy greater than combining atomic orbitals* **(anti-bonding orbitals).**

(v) *The shapes of the molecular orbitals depend upon the shapes of combining atomic orbitals.*

(vi) *The molecular orbitals are filled in the increasing order of their energies, starting with the orbital of least energy* **(Aufbau rule).**

(vii) *A molecular orbital like atomic orbitals can accommodate only two electrons and these electrons must have opposite spin* **(Pauli's principle).**

(viii) *While filling molecular orbitals of equal energy pairing of electrons does not take place until all such orbitals are singly occupied* **(Hund's rule).**

1.13. LINEAR COMBINATION OF ATOMIC ORBITALS (LCAO) METHOD

Molecular orbitals are formed by the combination of atomic orbitals of bonded atoms. In wave mechanics atomic orbitals are expressed by wave functions (ψ's). These wave functions are obtained as the solutions of Schrödinger wave equation. Just like atomic orbitals, Schrödinger wave equation can be written to describe the behaviour of the electron in molecules also. However, because of the complex nature of the

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Schrödinger wave equation it may not be easy to solve it for molecules. Thus in view of it, for the sake of convenience, the researchers applied an approximate technique to obtain the wave functions for molecular orbitals. This approximate method is known as *linear combination of atomic orbitals (LCAO) method.*

Let us apply this theory to homonuclear diatomic molecules such as hydrogen molecule. Let us consider the two atoms of hydrogen in the molecule as A and B. Each hydrogen atom has one electron in 1*s* orbital in ground state. These atomic orbitals may be represented by the wave functions ψ_A and ψ_B. Then according to LCAO method, the molecular orbitals in the H_2 molecule are given by linear combination (addition or subtraction of wave functions of the individual atoms) of ψ_A and ψ_B as shown below :

$$\psi_{MO} = \psi_A \pm \psi_B$$

$$\psi_b = \psi_A + \psi_B$$

$$\psi_a = \psi_A - \psi_B$$

The molecular orbital ψ_b formed by the addition overlap (*constructive interference of waves*) of atomic orbitals is called **bonding molecular orbital** and the molecular orbital ψ_a formed by the subtraction overlap (*destructive interference of waves*) of atomic orbitals is called **anti-bonding molecular orbital**.

The **formation of bonding and anti-bonding** orbitals can also be interpreted in terms of sign of wave functions of the orbitals which interact. Since a wave possesses a *crest* and *a trough* therefore the *positive* and *negative* signs are arbitrarily assigned to the crest and trough respectively.

In order to understand it let us consider the interference of waves. Now if the crest of one wave overlaps with the crest of the other, the two waves interact in a *constructive inference* and therefore the new resulting wave is *reinforced i.e. add up.* In other words, there is *in phase overlap* or *addition overlap* [Fig. 1.16 (*a*)]. In the similar way, addition overlap of atomic orbitals with same signs leads to the formation of **bonding molecular orbital**. On the contrary, if the crest of one wave overlaps with the trough of the other, then two waves interact in a *destructive* manner. In other words, this is *out of phase overlap* or *subtraction overlap* and the resulting wave is weakened [Fig. 1.16 (*b*)]. Such type of subtraction overlap of atomic orbitals with opposite signs leads to the formation of **anti-bonding molecular orbital**.

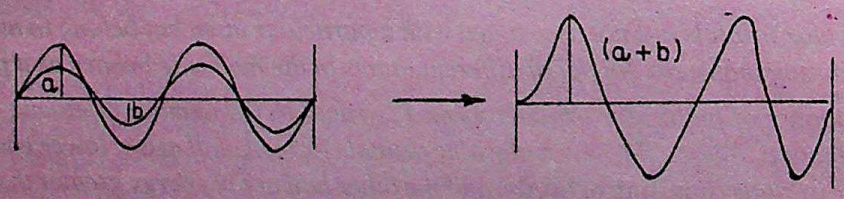

Fig. 1.16. (*a*) Constructive interference ; amplitudes are added up.

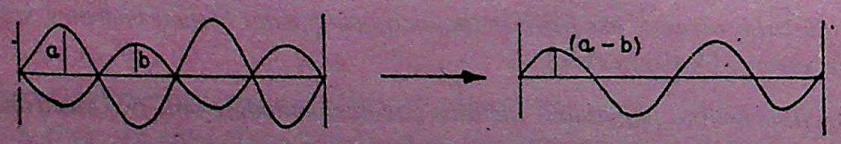

Fig. 1.16. (*b*) Descructive interference ; amplitudes are substracted.

The combination of 1*s* orbitals of hydrogen atoms to form molecular orbitals has been shown in Fig. 1.17.

As is clear from the figure, in the bonding molecular orbital the electron density is mainly concentrated in between the nuclei, so the electrons feel greater force of attraction in the orbital. Hence, bonding molecular orbital is of lower energy as compared to atomic orbitals. On the other hand, in the anti-bonding molecular orbital the electron density is mainly concentrated away from the nuclei ; in between the nuclei there is a node. So the electrons feel less force of attraction in this orbital and hence anti-bonding molecular orbital is of higher energy as compared to atomic orbitals.

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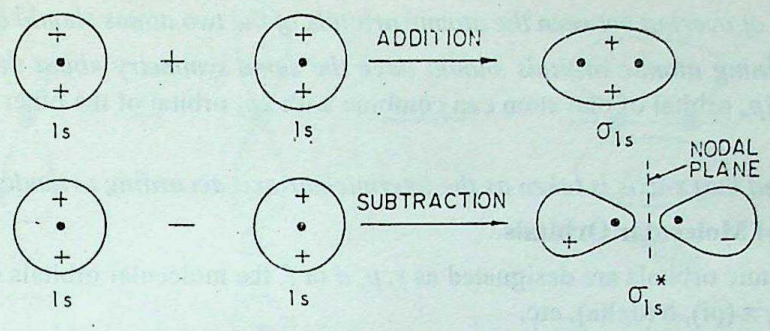

Fig. 1.17. Molecular orbitals formed by the combination of two 1*s* orbitals.

Relative energies of atomic orbitals and molecular orbitals in hydrogen molecule are shown in Fig. 1.18.

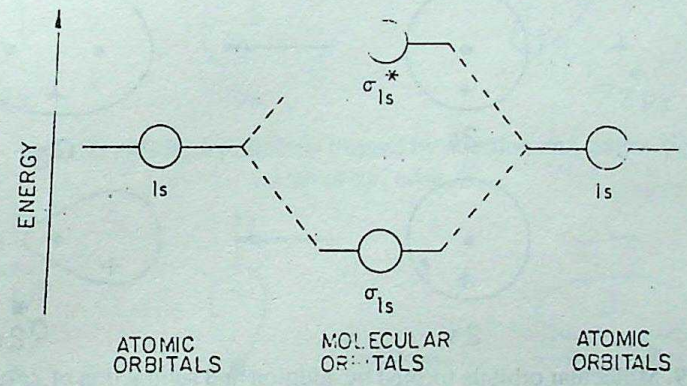

Fig. 1.18. Relative energies of bonding and anti-bonding molecular orbitals.

It may be noted that bonding molecular orbital is stabilized almost to the same extent as the anti-bonding molecular orbital is destabilized relative to atomic orbitals.

Differences Between Bonding and Anti-bonding Molecular Orbitals

Bonding M.O.	*Anti-bonding M.O.*
1. Bonding molecular orbital is formed by the addition overlap of atomic orbitals.	1. Anti-bonding molecular orbital is formed by the subtraction overlap of atomic orbitals.
2. It may or may not have a node.	2. It always has a node in between the nuclei of bonded atoms.
3. Electrons in this orbital lead to attraction between atoms.	3. Electrons in this orbital lead to repulsion between atoms.
4. Its energy is less than the energy of the atomic orbitals.	4. Its energy is more than the energy of the atomic orbitals.

Conditions for the Combination of Atomic Orbitals

For the atomic orbitals to combine resulting in the formation of molecular orbitals the main conditions are :

(*i*) *The combining atomic orbitals should have almost same energies.* For example, in case of homonuclear diatomic molecules 1*s* orbital of one atom can combine with 1*s* orbital of the other atom but 1*s* orbital of one atom cannot combine with 2*s* orbital of the other atom.

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(ii) *The extent of overlap between the atomic orbitals of the two atoms should be large.*

(iii) *The combining atomic orbitals should have the same symmetry about the molecular axis.* For example, $2p_x$ orbital of one atom can combine with $2p_x$ orbital of the other atom but not with $2p_z$ orbital.

It must be noted that z-axis is taken as the internuclear axis according to modern conventions.

Designation of Molecular Orbitals

Just as the atomic orbitals are designated as *s*, *p*, *d* or *f*, the molecular orbitals of diatomic molecules are named, σ (sigma), π (pi), δ (delta), etc.

σ-Molecular Orbitals. *The molecular orbitals which are cylindrically symmetrical around the internuclear axis are called sigma, σ-molecular orbitals.* For example, the molecular orbitals formed by

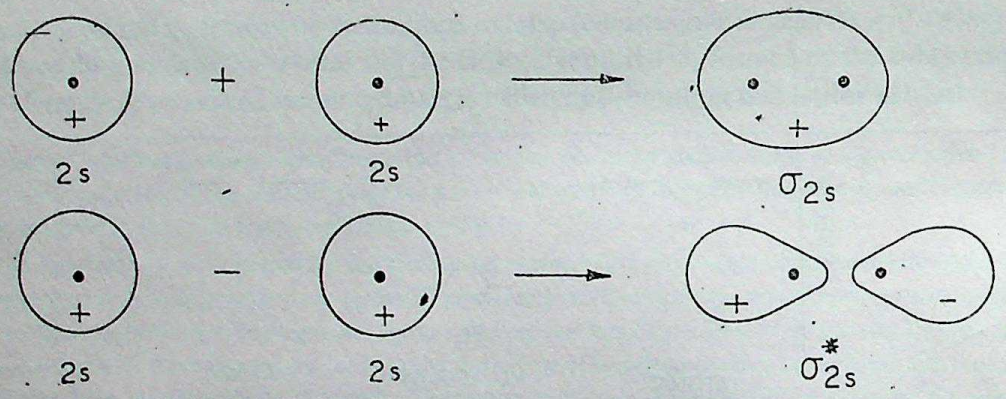

Fig. 1.19. Molecular orbitals formed by addition and subtraction of 2*s* orbitals.

addition of 1*s* orbitals is designated as σ_{1s} and the molecular orbital formed by subtraction of 1*s* orbitals is designated as σ_{1s}^* (Fig. 1.17). Similarly, combination of 2*s* orbitals results in the formation two sigma molecular orbitals designated as σ_{2s} and σ_{2s}^* as illustrated (Fig. 1.19).

Among 2*p* orbitals as the $2p_z$ orbital is assumed to lie along internuclear axis, therefore the molecular orbital formed by the addition overlap of $2p_z$ orbitals is designated as σ_{2p_z} while the molecular orbital formed by the subtraction overlap of $2p_z$ orbitals is designated of $\sigma_{2p_z}^*$ (Fig. 1.20).

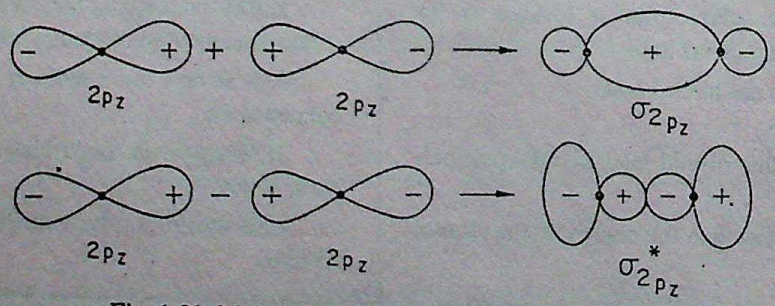

Fig. 1.20. Molecular orbitals formed by addition and subtraction overlap of $2p_z$ orbitals.

π-Molecular Orbitals. *The molecular orbitals which are formed by lateral overlap of p-orbitals are called pi (π) molecular orbitals.* For example, the addition and subtraction overlap of $2p_x$ orbitals result in the formation of π_{2p_x} and $\pi_{2p_x}^*$ molecular orbitals respectively as shown in Fig. 1.21.

Similarly, addition and subtraction overlap of $2p_y$ orbital results in the formation of π_{2p_y} and $\pi_{2p_y}^*$ orbitals respectively as illustrated in Fig. 1.22.

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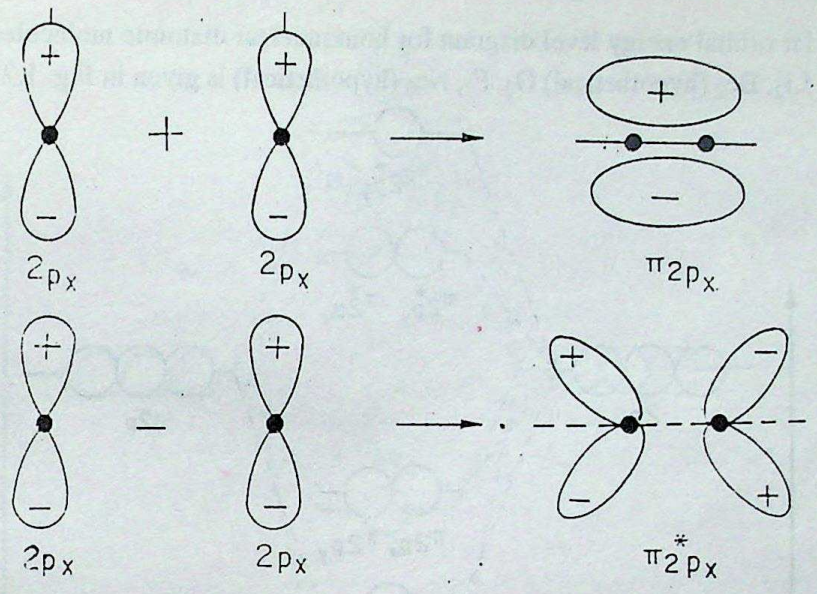

Fig. 1.21. Molecular orbitals formed by addition and subtraction overlap of $2p_x$ orbitals.

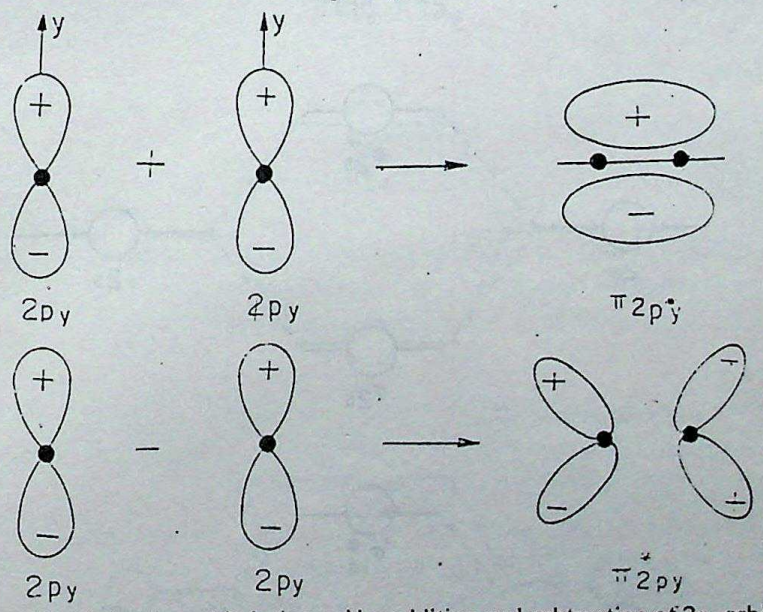

Fig. 1.22. Molecular orbitals formed by addition and subtraction of $2p_y$ orbitals.

1.14. ENERGY LEVEL DIAGRAM FOR MOLECULES

We have already learnt that combination of two 1*s* atomic orbitals of participating atoms form two new molecular orbitals designated as σ_{1s} and σ_{1s}^*. In the same manner, the 2*s* and 2*p* atomic orbitals, *i.e.*, eight atomic orbitals of two atoms give rise to eight new molecular orbitals *viz.*, σ_{2s}, σ_{2s}^* ; π_{2p_x} $\pi^*_{2p_x}$; π_{2p_y} $\pi^*_{2p_y}$; σ_{2p_z} $\sigma^*_{2p_z}$.

Increasing order of energies of various molecular orbitals is given below :

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < \sigma_{2p_z} < [\pi_{2p_x} = \pi_{2p_y}] < [\pi_{2p_x}^* = \pi_{2p_y}^*] < \sigma_{2p_z}^*$$

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The molecular orbital energy level diagram for homonuclear diatomic molecules like H_2, H_2^+, He_2^+, He_2 (hypothetical), Li_2, Be_2 (hypothetical) O_2, F_2, Ne_2 (hypothetical) is given in Fig. 1.23 (*a*).

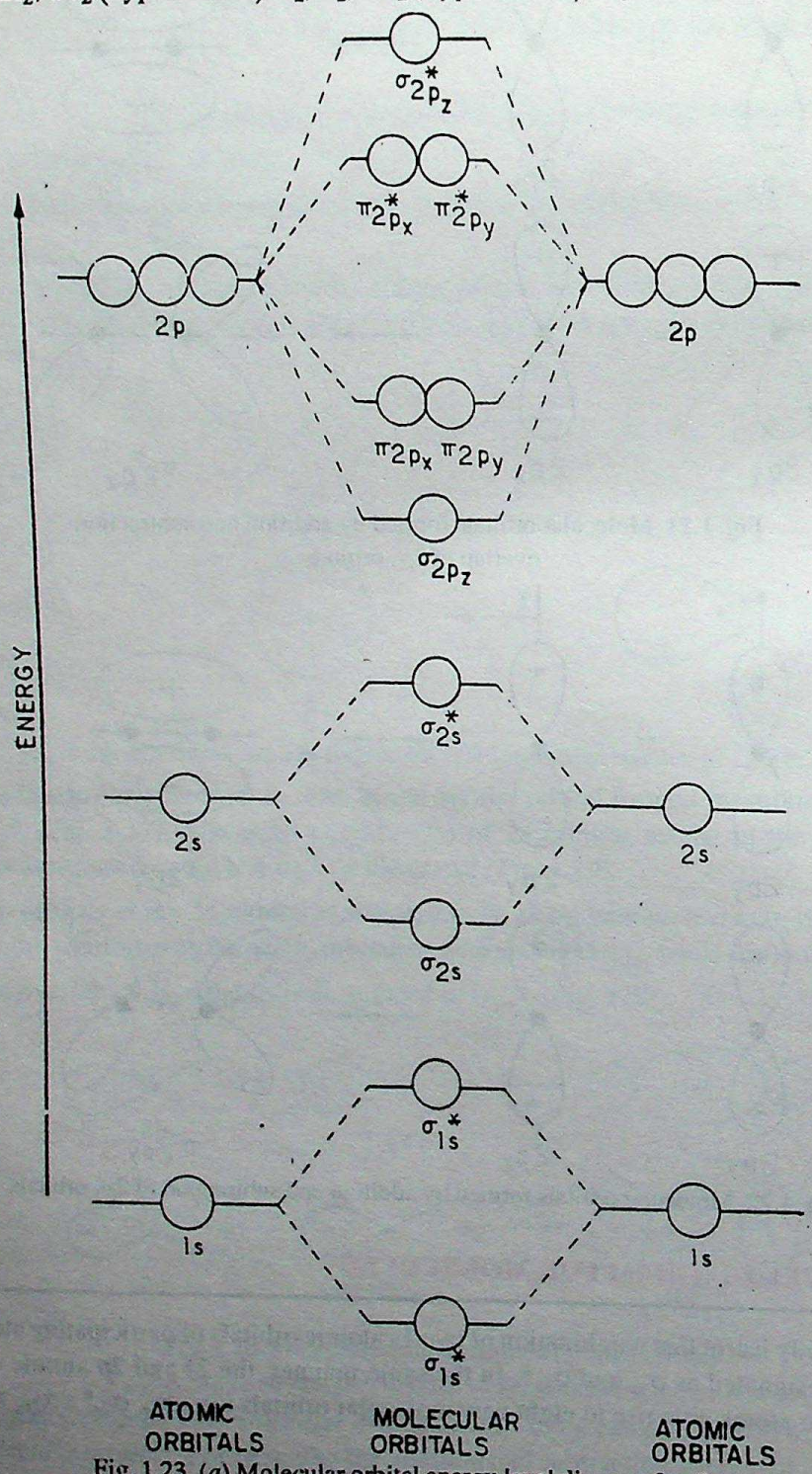

Fig. 1.23. (*a*) Molecular orbital energy level diagram for diatomic homonuclear molecules such as O_2, F_2, etc.

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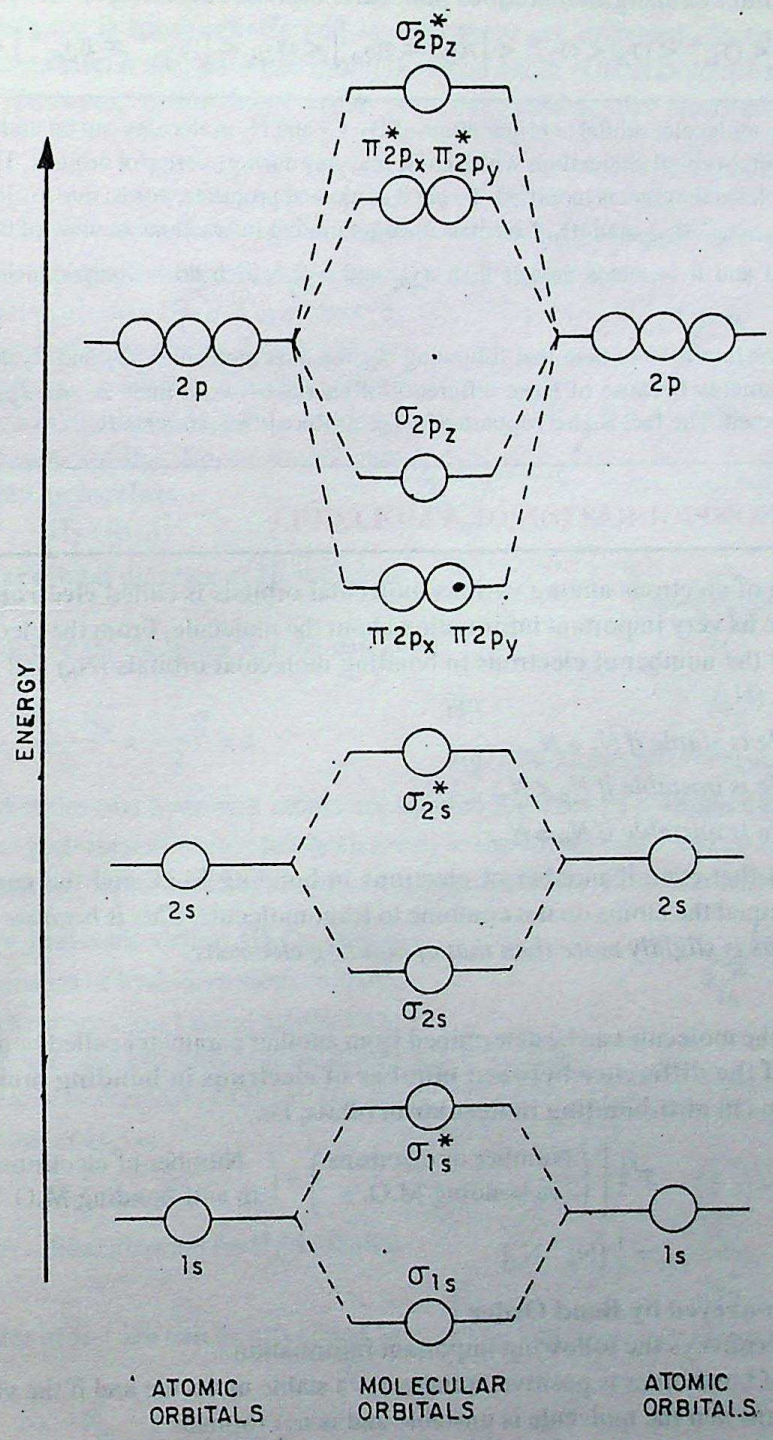

Fig. 1.23. (*b*) Molecular energy level diagram for diatomic homonuclear molecules such as N_2, C_2 and B_2.

However, the given sequence of energy levels of molecular orbitals is not correct for all the molecules. For instance, it has been observed experimentally that in some diatomic molecules such as B_2, C_2, N_2, etc. the molecular orbital energy level diagram shown in Fig. 1.23 (*b*) is followed. The important characteristic feature of the diagram is that the energy of σ_{2p_z} molecular orbital is higher than π_{2p_x} and π_{2p_y} molecular orbitals.

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The increasing order of energies of various molecular orbitals according to this diagram is

$$\sigma_{1s} < \sigma_{1s}^* < \sigma_{2s} < \sigma_{2s}^* < [\pi_{2p_x} = \pi_{2p_y}] < \sigma_{2p_z} < [\pi_{2p_x}^* = \pi_{2p_y}^*] < \sigma_{2p_z}^*.$$

The order for writing molecular orbital configurations of B_2, C_2 and N_2 molecules can be understood in terms of electron-electron or orbital-orbital interactions which come into play during overlap of orbitals. Thus, owing to these interactions the energy level diagram is modified. To put it in more appropriate words, due to close proximity of $2s$ and $2p_z$ orbitals, the σ_{2s}, σ_{2s}^* σ_{2p_z} and $\sigma_{2p_z}^*$ orbitals undergo mixing interactions in view of which the energy of σ_{2p_z} orbitals is raised and it becomes greater than π_{2p_x} and π_{2p_y} which do not experience these intermixing interactions.

It may be quite interesting to note here that following N_2, the next molecules, O_2 and F_2 do not exhibit these interactions. It is presumably because of large difference of energy between their $2s$ and $2p_z$ orbitals that such intermixing is insignificant. The fact is also supported by spectroscopic measurements.

1.15. ELECTRONIC CONFIGURATION OF A MOLECULE

The distribution of electrons among various molecular orbitals is called **electronic configuration** of the molecule. It can give us very important information about the molecule. From the electronic configuration it is possible to find out the number of electrons in bonding molecular orbitals (N_b) and number of electrons in anti-bonding orbitals (N_a).

(*i*) *The molecule is stable if* $N_b > N_a$.

(*ii*) *The molecule is unstable if* $N_b < N_a$.

(*iii*) *The molecule is unstable if* $N_b = N_a$.

It may be noted that even if number of electrons in bonding M.O. and the number of electrons in anti-bonding M.O. are equal the atoms do not combine to form molecule. *This is because of the fact that effect of anti-bonding electrons is slightly more than that of bonding electrons.*

Bond Order

The stability of the molecule can be determined from another parameter called bond order. **Bond order may be defined as half the difference between number of electrons in bonding molecular orbitals and the number of electrons in anti-bonding molecular orbitals,** *i.e.*,

$$\text{Bond order} = \frac{1}{2}\left[\begin{pmatrix}\text{Number or electrons}\\ \text{in bonding M.O.'s}\end{pmatrix} - \begin{pmatrix}\text{Number of electrons}\\ \text{in anti-bonding M.O.'s}\end{pmatrix}\right]$$

or

$$= \frac{1}{2}[N_b - N_a]$$

Information Conveyed by Bond Order :

The bond order conveys the following important information :

1. If the value of bond order is positive, it indicates a stable molecule and if the value of bond order is negative or zero, it means that the molecule is unstable and is not formed.

2. Dissociation energy of the molecule is direcly proportional to the bond order of the molecule. In other words, greater the bond order greater is the dissociation energy.

3. Bond length of the molecule is inversely proportional to the bond order of the molecule. In other words, greater the bond order shorter will be the bond length.

4. Knowing the bond order, the number of covalent bonds between the atoms in the molecule can be predicted. Bond order of a molecule is equal to the number of covalent bonds between the atoms in the molecule.

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5. The **magnetic behaviour of molecules** can also be predicted, *i.e.*, if all the electrons in a molecule are paired, the substance is **diamagnetic** and in case there are unpaired electrons in a molecule, the substance is **paramagnetic.** *It may be noted that if the bond order is fractional the molecule will definitely be paramagnetic. However, if the bond order is whole number the molecule may or may not be paramagnetic.*

1.16. BONDING IN SOME DIATOMIC MOLECULES

Let us discuss bonding in some homonuclear diatomic molecules.

(1) Hydrogen molecule (H_2). It is formed by the combination of two hydrogen atoms. Each hydrogen atom has one electron in 1*s* orbital. Therefore, in all there are two electrons in hydrogen molecule which are present in σ_{1s} molecular orbital. So electronic configuration of hydrogen molecule is

$$H_2 : (\sigma_{1s})^2$$

The molecular orbital diagram of H_2 molecule is shown in Fig. 1.24.

The bond order of H_2 molecule can be calculated as given below :

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-0}{2} = 1$$

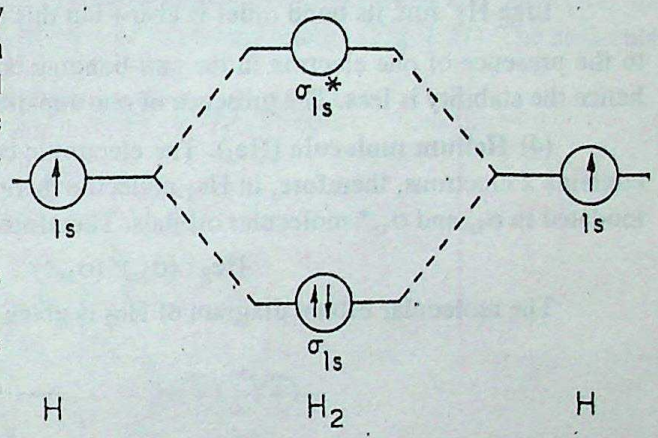

Fig. 1.24. Molecular orbital diagram of H_2 molecule.

This means that the two hydrogen atoms are bonded together by a **single covalent bond.** The bond dissociation energy of hydrogen molecule has been found to the 458 kJ mol^{-1} and bond length equal to 74 pm. Since no unpaired electron is present in hydrogen molecule, therefore, it is **diamagnetic.**

(2) Hydrogen molecule cation (H_2^+). This is formed by the combination of hydrogen atom containing one electron and hydrogen ion having no electron. Therefore, this molecule ion has only one electron. This electron is present in lowermost M.O., *i.e.*, σ_{1s}. So electronic configuration of H_2^+ is

$$H_2^+ : (\sigma_{1s})^1$$

The molecular orbital diagram for H_2^+ is shown in Fig. 1.25.

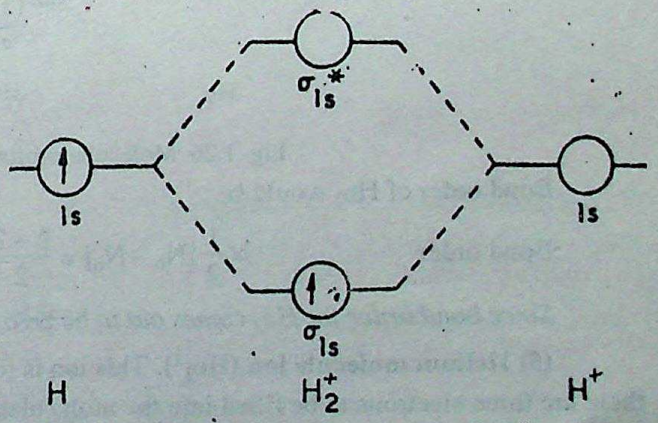

Fig. 1.25. Molecular orbital diagram of H_2^+ ion.

The bond order of H_2^+ ion can be calculated as given below :

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{1-0}{2} = \frac{1}{2}.$$

Since there is an unpaired electron in H_2^+ ion so it is expected to be **paramagnetic.** This fact has been confirmed experimentally. The bond length of H_2^+ ion is found to be 104 pm and its bond dissociation energy is found to be 269 kJ mol^{-1}. Bond length of H_2^+ ion is longer than that of H_2 molecule and its bond dissociation energy is smaller than that of H_2 molecule. This is due to its smaller bond order than that of H_2 molecule.

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(3) Hydrogen molecule anion (H_2^-). It is formed by the combination of hydrogen atom containing one electron and hydrogen negative ion containing two electrons. Accordingly, the M.O. configuration of the ion is

$$H_2^- : (\sigma_{1s})^2 (\sigma_{1s}^*)^1$$

The bond order of this ion, H_2^-, is

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-1}{2} = \frac{1}{2}.$$

Like H_2^+ ion, its bond order is also $\frac{1}{2}$ but this ion, H_2^-, is less stable than H_2^+ ion. This is attributable to the presence of one electron in the anti-bonding orbital due to which the destabilising effect is more and hence the stability is less. The presence of one unpaired electron in it makes it paramagnetic.

(4) Helium molecule (He_2). The electronic configuration of helium atom is $1s^2$. Each helium atom contains 2 electrons, therefore, in He_2 molecule there would be 4 electrons. These electrons will be accommodated in σ_{1s} and σ_{1s}^* molecular orbitals. Therefore, electronic configuration of He_2 would be

$$He_2 : (\sigma_{1s})^2 (\sigma_{1s}^*)^2.$$

The molecular orbital diagram of He_2 is given in Fig. 1.26.

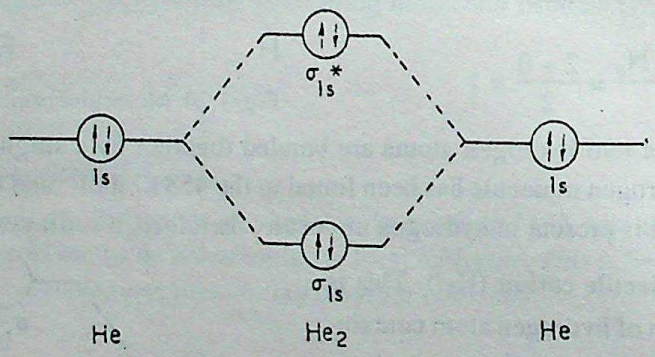

Fig. 1.26. Molecular orbital diagram of He_2 molecule.

Bond order of He_2 would be :

$$\text{Bond order} = \frac{1}{2}[N_b - N_a] = \frac{2-2}{2} = \text{zero}.$$

Since bond order for He_2 comes out to be zero, therefore this molecule is unstable and does not exist.

(5) Helium molecule ion (He_2^+). This ion is formed by combination of He atom and He^+ ions. Thus, there are three electrons to be filled into the molecular orbitals. The configuration of the ion is :

$$He_2^+ : (\sigma_{1s})^2 (\sigma^*_{1s})^1$$

The bond order is thus,

$$\text{Bond order} = \frac{N_b - N_a}{2} = \frac{2-1}{2} = \frac{1}{2}$$

As the bond order is positive, this ion is formed. Its bond dissociation energy is found to be 244 kJ mol^{-1}. Since there is one unpaired electron in it, the ion is paramagnetic in nature.

The molecular orbital configurations of Li_2, Be_2, B_2 and C_2 molecules alongwith the bond order and magnetic properties are given in Table 1.7.

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Table 1.7

Molecule	*M.O. configuration*	*Bond order*	*Magnetic character*
Li_2	$KK(\sigma_{2s})^2$	1	diamagnetic
Be_2	$KK(\sigma_{2s})^2(\sigma^*_{2s})^2$	Zero	—
B_2	$KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_x})^1(\pi_{2p_y})^1$	1	paramagnetic
C_2	$KK(\sigma_{2s})^2(\sigma^*_{2s})^2(\pi_{2p_x})^2(\pi_{2p_y})^2$	2	diamagnetic

(6) Nitrogen molecule (N_2). Each nitrogen atom has seven electrons. Thus, N_2 molecule has 14 electrons which are to be accommodated in orbitals in order of increasing energy (Fig. 1.27). The molecular orbital configuration of N_2 molecule is :

$$(\sigma_{1s})^2(\sigma_{1s}^*)^2(\sigma_{2s})^2(\sigma_{2s}^*)^2(\pi_{2p_x})^2(\pi_{2p_y})^2(\sigma_{2p_z})^2$$

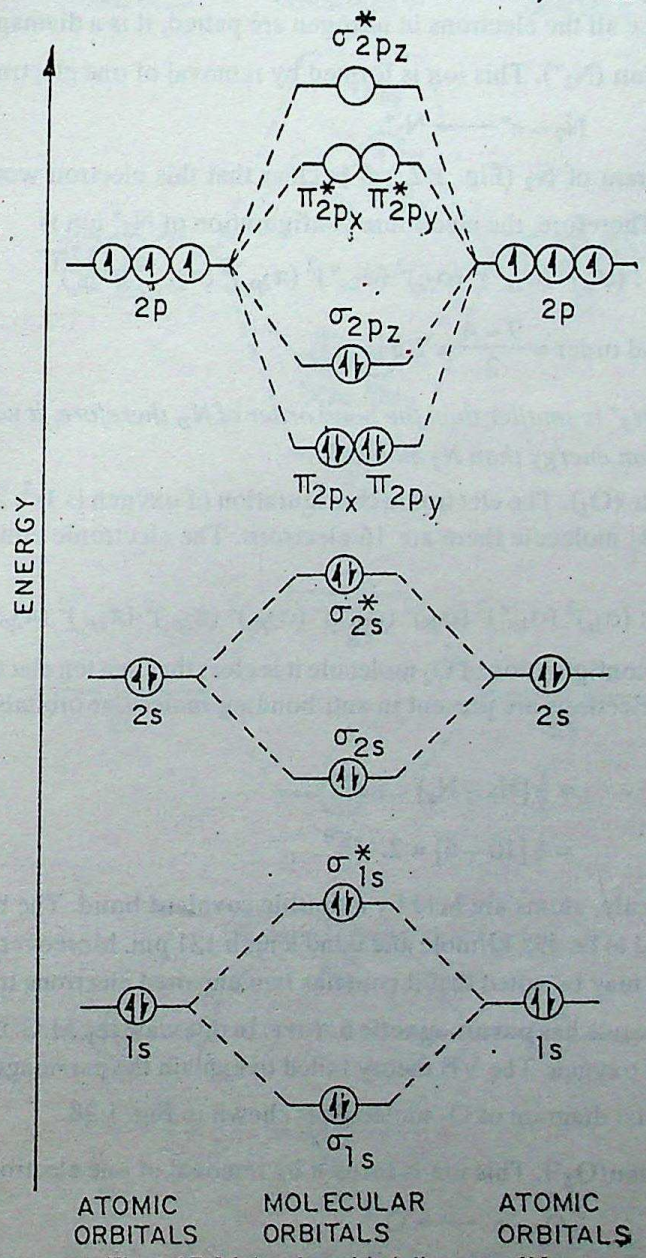

Fig. 1.27. Molecular orbital diagram of N_2

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Now, since the electrons filling the orbitals resulting by overlap of 1*s* orbitals have same number of bonding and anti-bonding electrons, therefore the bonding or anti-bonding effect of these orbitals can be neglected. Thus, the electrons of atoms in 1*s* orbital are represented by letter K. Therefore molecular orbital configuration of nitrogen can also be written as

$$N_2 : KK(\sigma_{2s})^2 (\sigma^*_{2s})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p_z})^2$$

It is evident that there are 10 bonding electrons and 4 anti-bonding electrons. Therefore, the bond order may be calculated as :

$$\text{Bond order} = \frac{1}{2}[N_b - N_a]$$
$$= \frac{1}{2}[10 - 4] = 3$$

The bond order suggests the bond energy to be very high. The experimental value of 945 kJ/mole is consistent with the fact. Since all the electrons in nitrogen are paired, it is a diamagnetic molecule.

Nitrogen molecule ion (N_2^+). This ion is formed by removal of one electron from N_2 molecule.

$$N_2 - e^- \longrightarrow N_2^+$$

From the M.O. diagram of N_2 (Fig. 1.27) it is clear that this electron would be removed from σ_{2p_z} bonding molecular orbital. Therefore, the electronic configuration of N_2^+ ion is

$$N_2^+ : (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\sigma_{2p_z})^1$$

$$\text{Bond order} = \frac{9-4}{2} = 2.5$$

Since bond order of N_2^+ is smaller than the bond order of N_2, therefore, it will have longer bond length and smaller bond dissociation energy than N_2 molecule.

(7) Oxygen molecule (O_2). The electronic configuration of oxygen is $1s^2, 2s^2, 2p^4$. Each oxygen atom has 8 electrons, hence, in O_2 molecule there are 16 electrons. The electronic configuration of O_2 molecule, therefore, is

$$O_2 : (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^1 (\pi_{2p_y}^*)^1$$

From the electronic configuration of O_2 molecule it is clear that in it ten electrons are present in bonding molecular orbitals and six electrons are present in anti-bonding molecular orbitals. Its bond order, therefore, is

$$\text{Bond order} = \frac{1}{2}[N_b - N_a]$$
$$= \frac{1}{2}[10 - 6] = 2.$$

So in oxygen molecule, atoms are held by a **double covalent bond.** The bond dissociation energy of O_2 molecule has been found to be 495 kJ/mole and bond length 121 pm. Moreover, from the molecular orbital diagram of O_2 molecule, it may be noted that it contains two unpaired electrons in $\pi_{2p_x}^*$ and $\pi_{2p_y}^*$ molecular orbitals. Therefore, O_2 molecule has **paramagnetic nature.** In this way, the M.O. theory successfully explains the paramagnetic nature of oxygen. The VB theory failed to explain the paramagnetic nature of oxygen.

The molecular orbital diagram of O_2 molecule is shown in Fig. 1.28.

Oxygen molecule ion(O_2^+). This ion is formed by removal of one electron from O_2 molecule.

$$O_2 - e^- \longrightarrow O_2^+$$

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From the M.O. diagram (Fig. 1.28) of O_2 it is clear that this electron would be removed from one of the anti-bonding molecular orbitals ($\pi_{2p_x}{}^*$ or $\pi_{2p_y}{}^*$). Therefore, the electronic configuration of O_2^+ ion is

$$O_2^+ : (\sigma_{1s})^2 (\sigma_{1s}{}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}{}^*)^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}{}^*)^1$$

and its bond der is $= \frac{10-5}{2} = \frac{5}{2} = 2.5.$

Since l ɔnd order of O_2^+ is greater than the bond order of O_2, therefore, it will have smaller bond length and greater bond dissociation energy than that of O_2 molecule. Its bond length is 112 pm and bond dissociation energy is 625 kJ/mole. Moreover, because of the presence of an unpaired electron, it is expected to be **paramagnetic**.

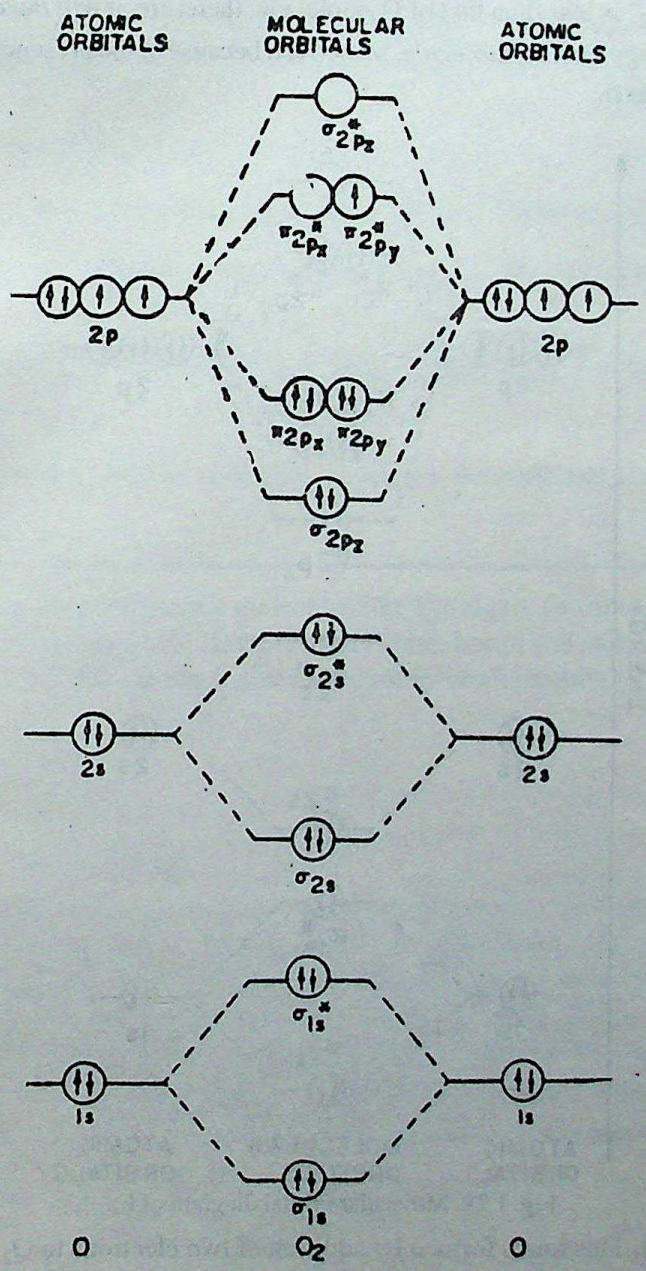

Fig. 1.28. Molecular orbital diagram of O_2 molecule.

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Superoxide ion (O_2^-). This ion is formed by addition of one electron to O_2 molecule.

$$O_2 + e^- \longrightarrow O_2^-$$

This additional electron enters into one of the anti-bonding orbitals ($\pi_{2p_x}^*$ or $\pi_{2p_y}^*$). Therefore, electronic configuration of O_2^- ion is

$$O_2^- : (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^2 (\pi_{2p_y}^*)^1$$

and its bond order is $= \frac{10-7}{2} = \frac{3}{2} = 1\frac{1}{2}$.

Since bond order of O_2^- is less than that of O_2 molecule, therefore, *it will have longer bond length and smaller bond dissociation energy than O_2 molecule.* Moreover, because of the presence of an unpaired electron, it is expected to be **paramagnetic**.

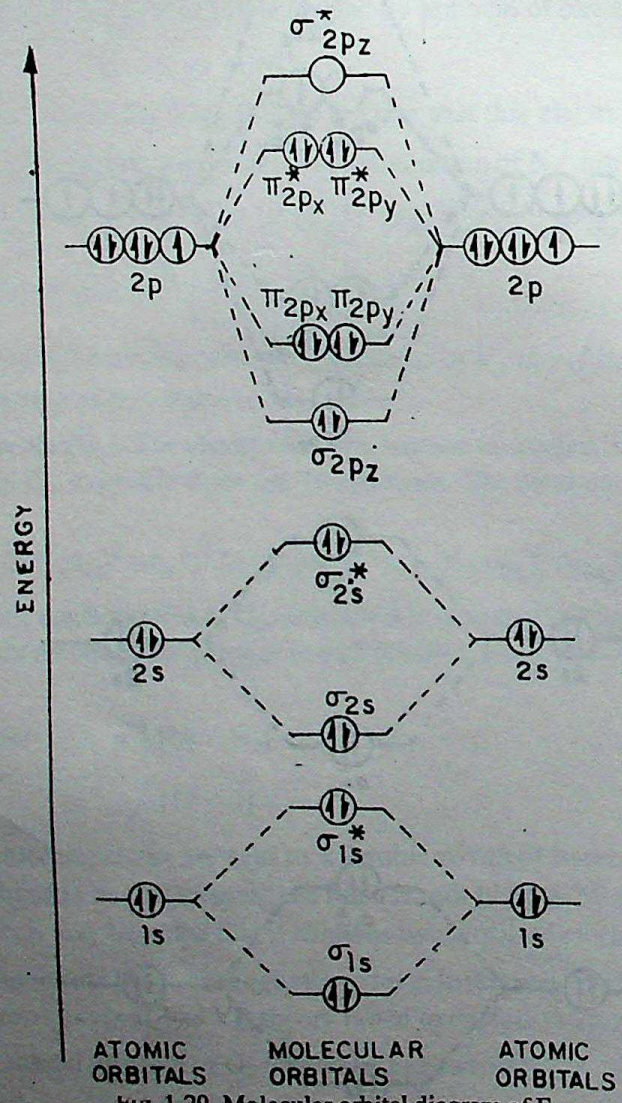

Fig. 1.29. Molecular orbital diagram of F_2.

Peroxide ion (O_2^{2-}). This ion is formed by addition of two electrons to O_2 molecule.

$$O_2 + 2e^- \longrightarrow O_2^{2-}$$

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These additional electrons enter the two half-filled π anti-bonding orbitals. Therefore, electronic cofiguration of O_2^{2-} ion is

$$O_2^{2-} : (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^2 (\pi_{2p_y}^*)^2$$

and its bond order is $= \frac{10-8}{2} = 1$.

Since bond order of O_2^{2-} ion is less than that of O_2 molecule, therefore, *it will have longer bond length and smaller bond dissociation energy than that of O_2 molecule.* Since there is no unpaired electron in it, it is expected to be **diamagnetic.**

(8) Fluorine molecule (F_2). Fluorine atom has electronic configuration $1s^2$, $2s^2$, $2p^5$. There are total eighteen electrons (nine from each fluorine atom) to be filled in M.O.'s of F_2 molecule. The molecular orbital configuration of F_2 is

$$F_2 : (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^2 (\pi_{2p_y}^*)^2$$

and its **bond order is** $\frac{1}{2}(10-8) = 1$. It is diamagnetic since it has no unpaired electrons (Fig. 1.29).

(9) Neon (Ne_2). The 20 electrons in this molecule can be distributed into five bonding and five anti-bonding orbitals.

$$Ne_2 : (\sigma_{1s})^2 (\sigma_{1s}^*)^2 (\sigma_{2s})^2 (\sigma_{2s}^*)^2 (\sigma_{2p_z})^2 (\pi_{2p_x})^2 (\pi_{2p_y})^2 (\pi_{2p_x}^*)^2 (\pi_{2p_y}^*)^2 (\sigma_{2p_z}^*)^2$$

Bond order $= \frac{1}{2}(10-10) = 0$

Since bond order for Ne_2 comes out to be zero, hence it is unstable and does not exist.

1.17. HYBRIDISATION

The formation of a number of diatomic molecules like hydrogen, chlorine, fluorine, etc., could easily be explained by the valence bond approach. However, beryllium, boron and carbon provide some interesting cases of compound formation. The **ground state** electronic configurations of these elements are given below :

Beryllium, $_4Be = 1s^2 2s^2$

Boron, $_5B = 1s^2 2s^2 2p_x^1$

Carbon, $_6C = 1s^2 2s^2 2p_x^1 2p_y^1$

A look at these electronic configurations reveals that beryllium has no unpaired electrons, therefore, it should not form any compound. Similarly, boron which has only one half-filled orbital and carbon which has two half-filled orbitals should behave as monovalent and bivalent elements in their compounds. But contrary to this we find beryllium to be bivalent in its compounds like BeF_2, $BeCl_2$. Boron, on the other hand, forms compounds like BF_3 and BCl_3 whereas carbon is invariably tetracovalent in its compounds.

In order to explain the formation of the compounds of beryllium, boron and carbon the idea of **promotion and hybridisation** has to be introduced. The basic utility of this purely theoretical concept is to account for :

(*i*) *observed valencies,*

(*ii*) *equivalence of bonds,* and

(*iii*) *observed bond angles.*

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In all the above cases in order to explain the observed valencies of 2, 3 and 4 for Be, B and C respectively, it is presumed that the electron in the 2*s* orbital gets unpaired and is promoted to vacant 2*p* orbital. The **excited state** electronic configurations of these elements are :

Beryllium, $_4Be = 1s^2 2s^1 2p_x^1$

Boron, $_5B = 1s^2 2s^1 2p_x^1 2p_y^1$

Carbon, $_6C = 1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$

Since in the excited states, Be, B and C have 2, 3 and 4 unpaired electrons, therefore, they exhibit valencies of 2, 3 and 4 respectively. Further, to account for the equivalence of bonds, it is proposed that before bond formation, redistribution of energies takes place between orbitals having slightly different energies resulting in the formation of orbitals of equivalent energy and identical shape. The new orbitals formed are called hybrid orbitals and this concept is called hybridisation. Thus, **hybridisation** may be stated as :

The intermixing and redistribution of energies of orbitals of an atom having slightly different energies resulting in the formation of orbitals of equivalent energy and identical shape.

Salient Features of Hybridisation

(*i*) The orbitals undergoing hybridisation should have almost equal energies.

(*ii*) The number of hybrid orbitals formed is equal to the number of atomic orbitals participating in hybridisation.

(*iii*) The hybrid orbitals formed are always equivalent in energy and identical in shape.

(*iv*) The hybrid orbitals form more strong bonds than the unhybridised atomic orbitals due to better overlapping of hybrid orbitals.

(*v*) Both filled and half-filled orbitals can get hybridised.

(*vi*) Orbitals involved in π-bond formation are not hybridised.

Depending upon the number and type of atomic orbitals undergoing intermixing, hybridisation can be of different types. Shape of the molecule depends upon the state of hybridisation of the central atom. Different types of hybridisation and the corresponding shapes of the molecules are given in Table 1.8.

Hybridisation involving s and p orbitals

Depending upon different combinations of *s* and *p* orbitals three types of hybridisation are known. These are as follows :

1. **sp-hybridisation or diagonal hybridisation.** This involve hybridisation of one *s* and one *p*-orbital forming two *sp*-hybrid orbitals which are linearly oriented at an angle of 180°.

2. **sp^2-hybridisation or trigonal hybridisation.** This involves hybridisation of one *s* and two *p*-orbitals to form three sp^2 hybrid orbitals oriented at angle of 120°.

3. **sp^3-hybridisation or tetrahedral hybridisation.** This involves hybridisation of one *s* and three *p*-orbitals to form four sp^3 hybrid orbitals pointing along the corners of regular tetrahedron at angle of 109°.28′.

The detailed discussion of *sp*, sp^2 and sp^3-hybridisation have been discussed in class XI.

Hybridisation involving s, p and d-orbitals

1. sp^3d Hybridisation

In this type of hybridisation one *s*, three *p* and one *d* orbitals undergo hybridisation to form five sp^3d hybrid orbitals which are directed towards the five corners of a trigonal bipyramid.

In order to understand sp^3d hybridisation, let us consider the formation of PCl_5 molecule. The ground state electronic configuration of phosphorus atom may be represented as

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$$_{15}P \quad : \quad 1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$$
(ground state)

In order to explain the penta covalency of phosphorus it is assumed that under the conditions of bond formation the 3*s* electrons get unpaired and one of it is promoted to vacant $3d_z^2$ orbital. The excited state configuration of phosphorus may be represented as follows :

$$_{15}P \quad : \quad 1s^2 2s^2 2p^6 3s^1 3p_x^1 3p_y^1 3p_z^1 3d^1_{z^2}$$
(excited state)

Now there are five orbitals, one *s*, three *p* and one *d* orbital which are half-filled. These orbitals then hybridise to yield a set of five sp^3d hybrid orbitals, which point towards the five corners of a trigonal bipyramid (Fig. 1.30).

Three of these hybrid orbitals are oriented towards the three corners of an equilateral triangle making an angle of 120° between them. The remaining two hybrid orbitals are oriented at right angles to these three

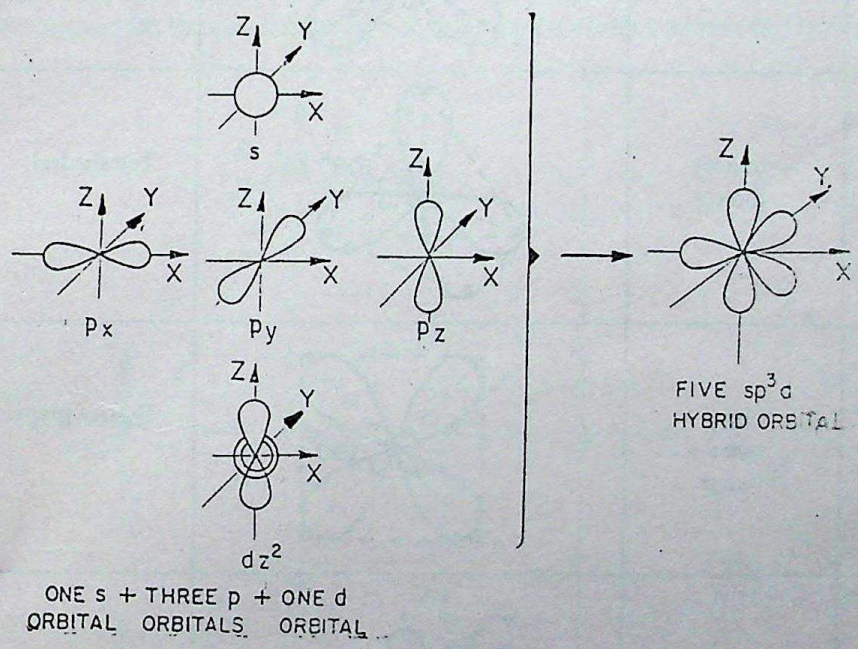

Fig. 1.30. The formation of five sp^3d hybrid orbitals.

orbitals. In PCl_5, these five sp^3d orbitals of phosphorus overlap with half-filled orbitals of chlorine atoms to form five P—Cl sigma bonds. Three P—Cl bonds lie in one plane and make an angle of 120° with each other. These bonds are called **equatorial bonds.** The two remaining P—Cl bonds are perpendicular to the plane of equatorial bonds *i.e.*, one above the plane and the other below the plane. These bonds are called **axial bonds.** As the axial bond pairs suffer more repulsive interactions from the equatorial bond pairs, therefore, to minimize them the axial bonds slightly elongate. Now as the axial bonds are slightly longer, therefore, these are weaker than equatorial bonds. Because of weaker axial bonds, PCl_5 is quite reactive.

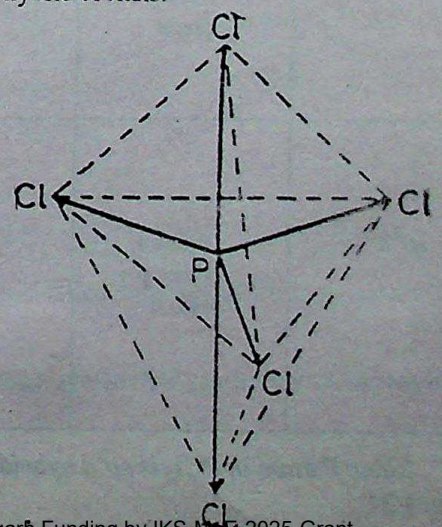

Fig. 1.31. Trigonal bipyramidal geometry of PCl_5 molecule.

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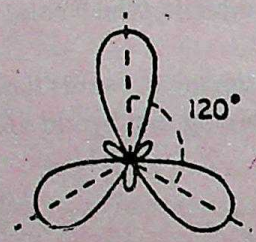
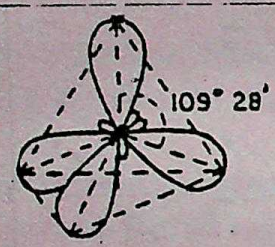
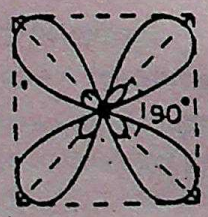
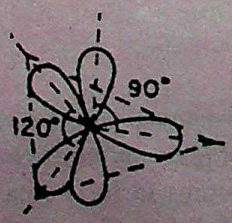
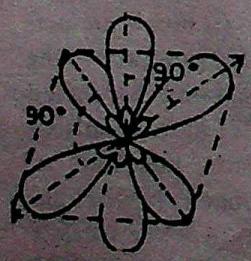
Table 1.8. Types of Hybridisation

Type of Hybridisation	*Atomic orbitals involved*	*Orientation of Hybrid orbitals*	*Shape of the molecule*	*Examples*
sp	one *s* + one *p*		Linear	BeF_2, $BeCl_2$, BeH_2, C_2H_2, $HgCl_2$
sp^2	one *s* + two *p*		Triangular planar	BF_3, C_2H_4, NO_3^-, CO_3^{2-}
sp^3	one *s* + three *p*		Tetrahedral	CH_4, CCl_4 NH_4^+
dsp^2	one *d* + one *s* + two *p*		Square planar	$[Ni(CN)_4]^{2-}$ $[Pt\ Cl_4]^{2-}$
sp^3d	one *s* + three *p* + one *d*		Trigonai bipyramidal	PF_5, PCl_5
sp^3d^2	one *s* + three *p* + two *d*		Octahedral	SF_6, $[Co(NH_3)_6]^{3+}$

Since P atom in PCl_5 is sp^3d hybridised, the shape of PCl_5 molecule is **trigonal bipyramidal** as shown in Fig. 1.31

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2. sp^3d^2 Hybridisation

In this type of hybridisation one *s*, three *p* and two *d* orbitals undergo intermixing to form six identical sp^3d^2 hybrid orbitals. These six orbitals are directed towards the corners of an octahedron.

In order to understand the sp^3d^2 hybridisation let us consider the formation of SF_6 molecule. The ground and excited state configurations of sulphur are represented as :

$$_{16}S \quad : 1s^2 2s^2 2p^6 3s^2 3p_x^1 3p_y^1 3p_z^1$$
(ground state)

$$_{16}S \quad : 1s^2 2s^2 2p^6 3s^1 3p_x^1 3p_y^1 3p_z^1 3d^1_{x^2-y^2} 3d^1_{z^2}$$
(excited state)

In the excited state *i.e.*, under conditions of bond formation the 3*s* and 3*p* electrons get unpaired and one electron out of each pair is promoted to vacant $3d_{x^2-y^2}$ and $3d_{z^2}$ orbitals. Now there are six orbitals ; one *s*, three *p* and two *d* orbitals which are half-filled. These then hybridise to form six new sp^3d^2 hybrid orbitals which are projected towards the six corners of a regular octahedron as shown in Fig. 1.32.

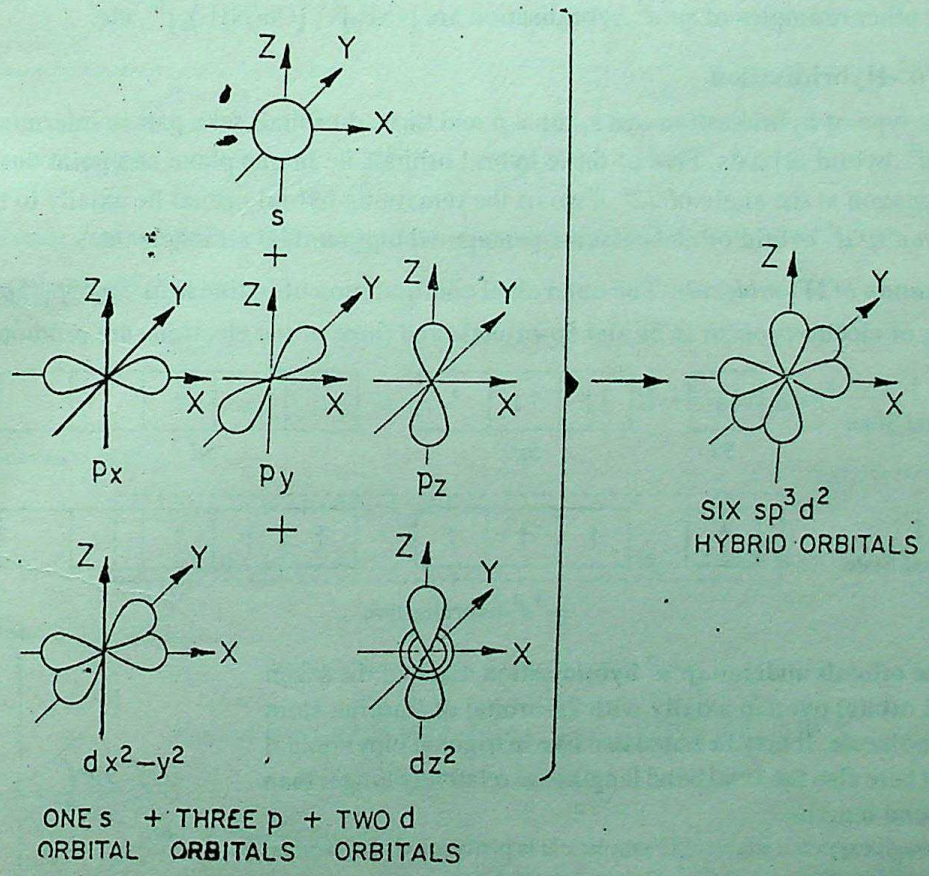

Fig. 1.32. The formation of six sp^3d^2 hybrid orbitals.

In SF_6, these six sp^3d^2 hybrid orbitals overlap with half-filled orbitals of fluorine atoms to form six S—F sigma bonds.

Because of sp^3d^2 hybridisation of sulphur, SF_6 has **regular octahedral geometry** as shown in Fig. 1.33. All the six S—F bonds in SF_6 have same bond length.

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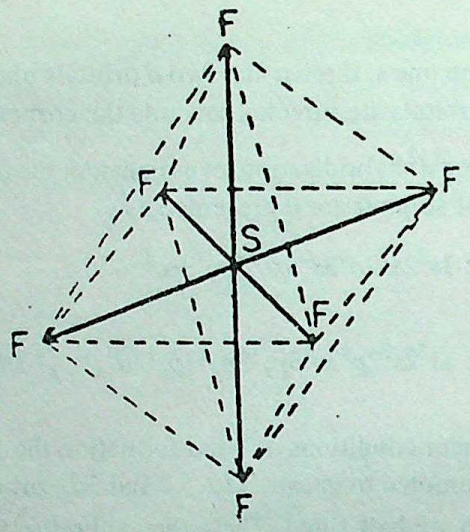


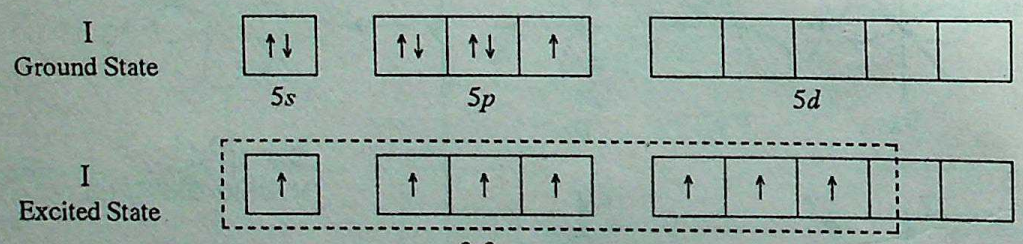
Fig. 1.33. Octahedral geometry of SF_6 molecule.

Some other examples of sp^3d^2 hybridisation are $[CrF_6]^{3-}$, $[Co(NH_3)_6]^{3+}$, etc.

3. sp^3d^3-Hybridisation

In this type of hybridisation one *s*, three *p* and three *d*-orbitals take part in intermixing to form seven identical sp^3d^3 hybrid orbitals. Five of these hybrid orbitals lie in one plane and point out along the corners of regular pentagon at the angle of 72°. Two of the remaining hybrid orbital lie axially to these five orbitals. Thus, the seven sp^3d^3 hybrid orbitals assume pentagonal bipyramidal arrangement.

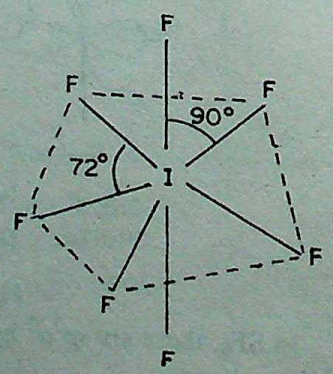
Formation of **IF_7** *molecule.* The outer shell configuration of iodine is $5s^2 5p_x^2 5p_y^2 5p_z^1$. In excited state the unpairing of electrons occur in 5*s* and 5*p*-orbitals and three of the electrons are promoted to 5*d*-orbitals.



sp^3d^3-hybridisation

These orbitals undergo sp^3d^3 hybridisation. Each of the seven sp^3d^3 hybrid orbital overlap axially with 2*p*-orbital of fluorine atom to form IF_7 molecule. It may be noted that like in trigonal bipyramidal arrangement here also the axial bond lengths are relatively longer than equatorial bond lengths.

Although expected shape of IF_7 molecule is pentagonal bipyramidal but spectroscopic analysis donot provide confirmation to this :



Pentagonal bipyramidal geometry

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PREDICTING THE HYBRID STATE OF THE ATOM IN DIFFERENT SPECIES

The hybrid state of the central atom in covalent molecules or ionic species other than complex ions can be predicted by following method. Various steps are :

1. Locate the central atom.
2. Find the number of surrounding atoms or groups and indicate them as **SA**.
3. Find the number of outer shell electrons in the central atom in ground state and indicate them as **G**.
4. Find the valency of the central atom in the given species. It is equal to the number of monovalent groups like H (OH), Cl, F, etc., or double the number of divalent groups like O, S, etc., directly linked to central atom. Indicate valency to be **V**.
5. Find electrical charge if species is ionic . Let it be represented by **E**.
6. Find the value of X by using the formula

$$X = SA + \frac{1}{2}(G - V \pm E)$$

Use + sign with E for **anions** and – sign with E for **cations**

Value of X	2	3	4	5	6	7
Hybrid state of central atom	sp	sp^2	sp^3	sp^3d	sp^3d^2	sp^3d^3

Note. *The above formula should not be used to predict the hybrid state of metal atoms in complex ions.*

Illustrations. (*i*) **Hybrid state of B in BF_4^-**

Here, SA = 4, G = 3 ; V = 4 ; E = 1

$\therefore$ $X = 4 + \frac{1}{2}(3 - 4 + 1) = 4$ $\therefore$ Hybrid state is sp^3

(*ii*) **Hybrid state of S in SO_2**

Here, SA = 2 ; G = 6 ; V = 4 ; E = 0

$X = 2 + \frac{1}{2}(6 - 4 + 0) = 3$ $\therefore$ Hybrid state is sp^2

(*iii*) **Hybrid state of Cl in ClF_3**

Here, SA = 3 ; G = 7 ; V = 3 ; E = 0

$X = 3 + \frac{1}{2}(7 - 3 + 0) = 3 + 2 = 5$ $\therefore$ Hybrid state is sp^3d

(*iv*) **Hybrid state of I in IO_3^-**

Here, SA = 3 ; G = 7 ; V = 6 ; E = 1

$X = 3 + \frac{1}{2}(7 - 6 + 1) = 4$ $\therefore$ Hybrid state is sp^3

(*v*) **Hybrid state of S in SO_4^{2-}**

Here, SA = 4 ; G = 6 ; V = 8 ; E = 2

$X = 4 + \frac{1}{2}(6 - 8 + 2) = 4$ $\therefore$ Hybrid state is sp^3.

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IMPORTANT TERMS, CONCEPTS AND FORMULAE

- **Photoelectric Effect :** Ejections of electrons from the surface of a metal by irradiating it with light of suitable frequency.

  Maximum K.E. of photoelectrons $= h\nu - h\nu^\circ = h(\nu - \nu^\circ)$

  $$= \frac{hc}{\lambda} - \frac{hc}{\lambda^\circ} = hc\left(\frac{1}{\lambda} - \frac{1}{\lambda^\circ}\right)$$

- **Planck's Quantum Theory :**

  Energy of photon, $E = h\nu$

  $$E = \frac{hc}{\lambda}$$

  Mass of photon, $m = \frac{h}{c\lambda}$

- **Dual Nature of Radiation :** Particle nature of radiation can account for photo-electric effect, reflection and refraction while wave nature of radiation can account for interference and diffraction.
- **Dual Nature of Matter (de Broglie Equation) :**

  $$\lambda = \frac{h}{mv}$$

  Wave character of matter has significance only for very small particles such as electrons, protons, neutrons, etc.

  Wave character of electrons was experimentally verified by **Davisson** and **Germer** by diffraction experiment.

- **Heisenberg's Uncertainty Principle :**

  $$\Delta x \times \Delta p \geq \frac{h}{4\pi}$$

  $$\Delta x \times m\Delta v \geq \frac{h}{4\pi}$$

- **Schrodinger Wave Equation :** An equation, derived by combining Planck's law ($E = h\nu$) and de Broglie equation $\left(\lambda = \frac{h}{mv}\right)$, to explain the behaviour of an electron in an atom.
- **Wave function (ψ) :** Refers to amplitude of electron wave. Square of wave function (ψ^2) determines the probability of an electron with a particular energy being present in a particular region.
- **Quantum Numbers :** Principal quantum number (n). Azimuthal quantum number (m), Magnetic quantum number (m) and Spin quantum number (s).

  Three quantum numbers n, l and m are needed to designate an orbital.

  Four quantum numbers n, l, m and s are required to designate an electron in an atom.
- **Principal quantum number (n)** determines the energy and the size of the orbital. Possible values of n are 1, 2, 3, ..., all whole number values.
- **Angular momentum quantum number (l)** determines shape of the orbital. Possible values of l for each value of n are 0, ... $(n - 1)$, all whole number values.
- **Magnetic quantum number (m)** determines the orientation of the orbital. Possible values of m for each value of l are all integral values from $-l$ ....., 0, ..., $+l$.
- **Energy of the electron in nth energy level of hydrogen atom is given by**

  $$E_n = -k^2 \frac{2\pi^2 me^4}{n^2h^2} = -\frac{2.178 \times 10^{-18}}{n^2} \text{ J/atom} = -\frac{1312}{n^2} \text{ kJ/mole}$$

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- **For nth energy level,** the maximum

  number of sub-shells = n

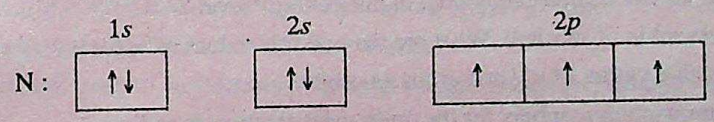
  number of orbitals = n^2

  number of electrons = $2n^2$
- **Ground state** of an atom corresponds to the lowest energy state of the atom.
- **Excited state :** An atom is said to be in excited state if some lower energy orbital is vacant and the electron is present in higher energy orbital. It is unstable state.
- **Electronic Configuration :** Distribution of electrons among various orbitals in an atom.

  Electronic configuration of an atom in ground state must obey the following three rules.

  Aufbau rule, Pauli's exclusion principle and Hund's rule of maximum spin multiplicity.
- **Aufbau Rule :** The orbitals are filled in the order of increasing energy, starting with the orbital of lowest energy.

  1s, 2s, 2p, 3s, 3p, 4s, 3d, 4p, 5s .....
- **Pauli's Exclusion Principles :** The basic requirement of this principle is that an electron can accommodate at the most two electrons and these electrons must have opposite spin.
- **Hund's Rule of Maximum Spin Multiplicity** states that pairing of electrons in orbitals of a particular subshell cannot take place until all the orbitals of the subshell are singly occupied. These singly occupied orbitals should have electrons with parallel spin.



- **Molecular Orbital Theory :** According to this theory, in molecules the electrons are present in new orbitals called molecular orbitals. Molecular orbitals are not associated with a particular atom but belong to nuclei of all the atoms constituting the molecule.
- **LCAO Method :** This is an approximate method, according to which the molecular orbitals are obtained by linear combination of atomic orbitals.
- **Bond Order** = $\frac{N_b - N_a}{2}$

  Species with fractional bond order are always paramagnetic.
- **O_2 molecule is paramagnetic** as it has two unpaired electrons.
- **N_2 molecule is diamagnetic** as it has no unpaired electrons.

EXERCISE

VERY SHORT ANSWER QUESTIONS
(1 Mark)

1. What type of metals are used in photoelectric cells ?
2. How is number of photoelectrons related to the intensity of light ?
3. Why non-metals do not exhibit photoelectric effect ?
4. What are the quantum numbers of the valence electrons in the magnesium atom in ground state ?
5. Do all p-electrons in nitrogen atom have same energy ? What is the effect of magnetic field on the energies of these electrons ?

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6. What are the possible values of magnetic quantum number for an electron in $4f$ sub-shell ?
7. Draw the shape of $2s$ orbital. How many nodes are there in it ?
8. How many spherical nodes are there in $4s$ sub-shell ?
9. Give the regions of maximum probability for $3p$ orbital.
10. What is uncertain in uncertainty principle ?
11. Is moving elephant associated with waves ? What is the physical significance of these waves ?
12. What are degenerate orbitals ? How many such orbitals are present in $5d$ sub-shell ?
13. Configuration of a carbon is $1s^2 . 2s^1 . 2p_x^1 . 2p_y^1 . 2p_z^1$. Is this atom in ground state ?
14. If uncertainty in momentum of an electron is zero, then what would be the uncertainty in its position ?
15. How do the three $2p$ orbitals differ from each other ?
16. Which d orbitals lie in xy plane ?
17. What is the number of unpaired electrons in Mn^{2+} ion ?
18. What is the number of d-electrons in Cr^{3+} ion ?
19. Which energy level in Li^{2+} has same energy as the fourth energy level of He^+ ion ?
20. Which quantum numbers determine size and shape of the orbital ?
21. Which of the following orbitals are not possible ?

$$3f, 4p, 2d, 3s.$$

22. What are the possible values of l for an electron in fourth energy level ?
23. How many electrons can be accommodated in third energy level ?
24. An electron is present in $5f$ subshell. What are the possible values of m for it ?
25. What are the possible values of n, l and m for $3p$ orbital ?
26. What are the four quantum numbers for the outer most electron in sodium ?
27. Give some points of difference between a $2p$ and a $3p$ orbital.
28. Is B_2 molecule paramagnetic in nature ?
29. Arrange N_2, O_2 and F_2 molecule in order of decreasing bond length.
30. Which two d-orbitals are involved in sp^3d^2 hybridisation in SF_6 ?
31. Why the energy of π_{2p_x} and π_{2p_y} orbitals is lower than σ_{2p_z} orbitals in the case of N_2 molecule ?
32. Which out of H_2^+ and H_2^- molecular ions is more stable and why ?
33. PCl_5 molecule is highly reactive, why ?
34. Write the electronic configuration for the element having atomic number 26. *(CBSE 1993)*
35. Calculate the bond order of He^+ molecular ion. *(CBSE 1993)*
36. Calculate the bond order of O^{2+} molecular ion. *(CBSE 1993)*
37. State Pauli's exclusion principle. *(CBSE 1994)*
38. Which quantum number specifies shape of an orbital. *(CBSE 1994)*
39. Give the equation which expresses the relationship between the wavelength (λ) and the momentum of a particle. *(CBSE 1994)*
40. What subshells would be found in the shell with $n = 4$? *(CBSE 1994)*
41. Write the state of hybridization of carbon in CO_3^{2-}. *(CBSE 1995)*
42. Write ground state electronic configuration of O_2^+. *(CBSE 1995)*
43. Write the state of hybridization of nitrogen in NO_3^- ion. *(CBSE 1995)*
44. Write the possible values of m for an electron with $l = 1$. *(CBSE 1995)*
45. Write the ground state electronic configuration of F_2^+. *(CBSE 1995)*
46. What is state of hybridisation in BF_3. *(CBSE 1996)*

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DESCRIPTIVE QUESTIONS
(2 or 3 Marks)

Dual Nature of Radiations

47. How did photoelectric effect indicate light is particulate in nature ?

48. What observations of photoelectric effect would not be explained by wave theory of radiations ?

49. What are the main points of Planck's quantum theory of radiation ?

50. What do you understand by photon of energy ? Which parameter determines the magnitude of photon ?

51. How does wave theory of radiation fail to explain the photoelectric effect ?

52. What is the relationship between energy of photon and wavelength of the radiation ?

53. What is the relation between maximum kinetic energy of the photo-electrons and the frequency of the incident radiations ?

54. What is the effect of increase in intensity of the incident light on the number of photo-electrons ejected per second and the maximum kinetic energy of photo-electrons ?

Dual Nature of Matter and Heisenberg's Uncertainty Principle

55. Derive an equation correlating the wavelength of a particle in motion to its momentum. Give the significance of this relationship.

56. What experimental evidence is available to show the dual nature of the electron ?

57. What are the differences between matter waves and light waves ?

58. Is it possible to define the exact path of an electron around the nucleus ? State and explain the principle upon which your answer is based.

59. What do you understand by wave function ψ ? What is its significance ?

60. How does uncertainty principle introduce concept of probability ?

61. State de Broglie equation. How would the wavelengths of moving objects vary with their masses ? ***(A.I. CBSE 1984)***

62. What is the limitation of de Broglie's equation ? How do matter waves differ from electromagnetic waves ?

63. Explain how an electron can be considered to have a particle as well as a wave nature. Give de Broglie equation for the wave-particle nature of matter.

64. Derive de Broglie equation for a particle of mass 'm' moving with a velocity 'c'. ***(A.I. CBSE 1985)***

Quantum Numbers

65. Name the quantum numbers required to designate an orbital in an atom.

66. Name the quantum numbers that determine the

(*i*) Size of orbital (*ii*) Shape of orbital.

67. How is energy of an electron in hydrogen atom related to the principal quantum number ?

68. What are the possible values of l for N-shell ? How are the corresponding subshells designated ?

69. What is the highest value of m for M-shell ? Explain.

70. Name various quantum numbers. What is the significance of principal quantum number ?

71. How can an atomic orbital be specified ? ***(CBSE 1982)***

72. Write the possible values of l and m for an electron in $4d$ orbital.

73. What are the n, l and m values for $2p_x$ and $3p_z$ electrons ?

74. Give possible values of n and l for an electron in

(*a*) $3p$ sub-shell (*b*) $3d$ sub-shell

(*c*) $4s$ sub-shell (*d*) $5f$ sub-shell.

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75. Can an electron have following set of quantum numbers ?

$$n = 3, l = 3, m = 3, s = +\frac{1}{2}.$$

76. Assign sets of quantum to all the electrons in the valence shell of nitrogen.

77. What is the significance of magnetic quantum number ?

78. Which of the following sets of quantum numbers are not allowed and why ?

(*i*) $n = 3 \quad l = 2 \quad m = +3 \quad s = +\frac{1}{2}$ (*ii*) $n = 4 \quad l = 4 \quad m = +2 \quad s = -\frac{1}{2}$

(*iii*) $n = 0 \quad l = 0 \quad m = 0 \quad s = +\frac{1}{2}$ (*iv*) $n = 3 \quad l = 2 \quad m = 0 \quad s = -\frac{1}{2}$

(*v*) $n = 4 \quad l = 0 \quad m = 0 \quad s = -\frac{3}{2}$.

79. What is the maximum number of electrons for the energy states designated by the quantum numbers :

(*i*) $n = 3$ (*ii*) $n = 3 \quad l = 2$? (*iii*) $n = 3 \quad l = 2 \quad m = +2$?

80. What is the number orbitals in

(*i*) Fourth energy level (*ii*) 5*f*-subshell ?

Atomic Orbitals

81. Draw and discuss the shapes of *d*-orbitals. ***(H.P. Board 1992)***

82. What is the number of spherical nodes in 3*s* orbital ? How does a 2*s* orbital differ from a 1*s* orbital ?

83. What is the maximum number of electrons that can be accommodated in

(*i*) third energy level (*ii*) 2*p* subshell (*iii*) a 4*f* orbital ?

84. What are degenerate orbitals ? Give an example of degenerate orbitals.

85. What is the order of energies of 4*s*, 4*p*, 4*d* and 4*f* orbitals in

(*i*) Hydrogen atom ? (*ii*) Chlorine atom ?

86. Draw probability density curve for

(*i*) 1*s* orbital (*ii*) 2*s* orbital

(*iii*) 2*p* orbital.

87. Draw plots of radial wave function for

(*i*) 1*s* orbital (*ii*) 2*s* orbital.

Electronic Configurations

88. Give the electronic configurations of Cu (atomic number 29) and justify your answer.

89. Write the electronic configuration of Mn (Z = 25) and Zn (At. No. 30).

90. State the explain Pauli's exclusion principle. What is the significance of word exclusion in it ?

91. Why half-filled and fully-filled electronic configurations possess extra-stability ?

92. Atomic number of potassium is 19. How many valence electrons are there in its atom ? In which shell are they ? ***(A.I. CBSE 1987 C)***

93. State Hund's rule of multiplicity. How is it used in the electron distribution of nitrogen (atomic number 7) ? ***(CBSE 1983)***

94. State Hund's rule of maximum multiplicity. What is its importance ? ***(A.I. CBSE 1986)***

95. What atoms are indicated by the following electronic configurations ?

(*i*) $1s^2, 2s^2, 2p_x^1, 2p_y^1, 2p_z^1$ (*ii*) $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$.

Are these atoms in their ground state or excited states ? ***(A.I. CBSE 1986)***

96. Write the electronic configurations of Cu^{2+} and Cr^{3+} ions given atomic numbers of Cu and Cr as 29 and 24 respectively. ***(A.I. CBSE 1985)***

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97. An atom has 2K, 8L and 5M electrons. Write down electronic configuration of the element and indicate in it :
(*i*) Number of subshells (*ii*) Number of orbitals
(*iii*) Number of unpaired electrons (*iv*) Number of *p*-electrons
(*v*) Number of electrons with $l = 0$.

98. Give the electronic configurations of the following ions :
(*i*) Fe^{2+} (*ii*) Fe^{3+} (*iii*) Cr^{3+}.
Which of these has maximum number of unpaired electrons ?

99. Which of the following electronic configurations are not allowed for the atoms in ground state ? Explain why.
(*i*) $1s^2, 2s^2, 2p_x^2$, (*ii*) $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5$
(*iii*) $1s^2, 2s^1, 2p_x^1, 2p_y^1, 2p_z^1$.

100. How many unpaired electrons are present in ground states of the following atoms ?
(*i*) O (*ii*) Ca (*iii*) V.

101. Why is the following electronic configuration not correct for ground state of chromium atom ?

$$1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 4s^2, 3d^4.$$

Molecular Orbital Theory

102. Discuss the main points of molecular orbital theory. What is basic difference between this theory and valence bond theory ?

103. What do you understand by sigma and pi molecular orbitals ?

104. Show the formation of molecular orbitals by the combination of
(*a*) $2p_z$ and $2p_z$, (*b*) $2p_x$ and $2p_x$, (*c*) $1s$ and $1s$
atomic orbitals and indicate how are they designated ?

105. What do you understand by bonding and anti-bonding molecular orbitals ? ***(A.I. CBSE 1986)***

106. Explain with the help of molecular orbital theory why H_2 exists and He_2 does not exist.

107. With the help of molecular orbital approach show that Ne_2 cannot exist as a stable species. ***(CBSE 1994)***

108. What do you understand by bond order of a molecule ? What is its significance ?

109. Why bonding molecular orbitals are more stable than anti-bonding molecular orbitals ?

110. How does molecular orbital theory explain the paramagnetic nature of oxygen ?

111. Give molecular orbital diagram of peroxide ion and calculate the bond order in it. Will it be paramagnetic ?

112. What is meant by bond order ? Calculate the bond order in He_2^+, O_2 and N_2 molecules.

113. Give the number of electrons which occupy the bonding molecular orbitals in H_2^+, H_2 and He_2.

114. What do you understand by a molecular orbital ? What is the maximum number of electrons that occupy a molecular orbital ? ***(H.P. 1992)***

115. Draw the molecular orbital diagram for the O_2 molecule and determine the bond order and the magnetic character therein. ***(A.I. CBSE 1982 ; CBSE 1985 ; Pb. 1991)***

116. Distinguish two aspects of the following :
(*a*) atomic and molecular orbitals (*b*) bonding and anti-bonding orbitals
(*c*) sigma and pi-bonds.

117. Is B_2 molecule paramagnetic in nature ?

118. Arrange N_2, O_2 and F_2 molecule in order of decreasing bond length.

119. Which two *d*-orbitals are involved in sp^3d^2 hybridisation in SF_6 ?

120. Why the energy of π_{2p_x} and π_{2p_y} orbitals is lower than σ_{2p_z} orbitals in the case of N_2 molecule ?

121. Which out of H_2^+ and H_2^- molecular ions is more stable and why ?

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122. Calculate the bond order of He_2^+ molecular ion. *(A.I. CBSE 1993)*

123. Calculate the bond order of O_2^+ molecular ion. *(CBSE 1993)*

124. Give some differences between valence bond theory and molecular orbital theory.

125. Write down electronic configuration of superoxide ion (O_2^-) and calculate its bond order.

Hybridisation

126. Describe sp^3d hybridisation by taking example of PCl_5.

127. Describe sp^3d^2 hybridisation with the help of some suitable example.

128. Explain why all the P-F bonds donot have same bond length in PF_5.

129. Draw the shapes and give the designation of the two *d* orbitals which participate in sp^3d^2 hybridisation.

130. Explain why all the S-F bonds have same bond length in SF_6.

131. Explain why PCl_5 dissociates to give PCl_3 and Cl_2.

132. Explain why PCl_5 is more reactive than PCl_3.

NUMERICAL PROBLEMS

133. The threshold wavelength for tungsten metal is 260 nm. What would be the maximum kinetic energy of photo-electrons when tungsten is irradiated with light of wavelength 220 nm ?

134. A radiostation is transmitting waves of 400 kHz frequency. If the distance between the radiostation and the receiver is 300 km, what time will the waves take to reach the receiver from the radio station ?

135. Calculate energy of one mole photons of radiation having wavelength 300 nm.

136. Calculate the number of photons of radiation having frequency 1×10^{15} Hz that can supply 1 kJ of energy.

137. Calculate the mass of a photon of light having wavelength 600 nm. $C = 3 \times 10^8$ m s^{-1} and Plancks constant, $h = 6.62 \times 10^{-34}$ kg m^2s^{-1}.

138. Two particles A and B are in motion. If the wavelength associated with particle A is 5×10^{-8} m, calculate the wavelength of the particle B if its momentum is half of A.

139. Calculate the wavelength of a 1000 kg rocket moving with a velocity of 300 km per hour. $h = 6.625 \times 10^{-34}$ Joules-sec. *(H.S.B. 1994)*

140. Calculate the de Broglie wavelength for an electron travelling at 1 per cent the speed of light. Mass of electron is 9.1×10^{-31} kg and the velocity of light is 3×10^8 ms^{-1}.

141. Calculate momentum of a particle which has de Broglie wavelength of 0.1 nm. ($h = 6.6 \times 10^{-34}$ kg m^2s^{-1}) *[CBSE (1) 1994]*

142. The kinetic energy of a sub-atomic particle is 5.45×10^{-25} J. Calculate the frequency of the particle wave. Planck's constant, ($h = 6.6 \times 10^{-34}$ kg m^2s^{-1}). *[A.I. CBSE (1) 1995]*

143. Calculate the product of uncertainty in position and uncertainty in velocity for electron. Mass of electron is 9.1×10^{-31} kg and Planck's constant $h = 6.62 \times 10^{-34}$ kg m^2s^{-1}.

144. The uncertainty in position of a moving bullet of mass 10 g is 10^{-5} m. Calculate the uncertainty in its velocity.

145. Calculate the wavelength of a photon emitted when the electron of hydrogen atom groups from the fourth shell *p* second shell. The ionisation energy of H atom is 1.312×10^3 kJ mol^{-1}. *(CBSE 1996)*

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select the correct answer from the following questions :

1. Which of the following metals will exhibit photoelectric effect most easily ?
(*a*) Sodium (*b*) Magnesium
(*c*) Caesium (*d*) Lithium.

2. Wave nature of electrons is shown by
(*a*) Photoelectric effect (*b*) Compton effect
(*c*) Diffraction experiment (*d*) Thomson effect.

3. The concept of Dual Nature of radiation was proposed by
(*a*) Max Planck (*b*) Einstein
(*c*) de Broglie (*d*) Heisenberg.

4. Which of the following relates to photons both as wave motion and as a stream of particles
(*a*) Interference (*b*) $E = mc^2$
(*c*) Diffraction (*d*) $E = h\nu$. ***(I.I.T. 1992)***

5. Neutrons can be found in atoms of all the elements except
(*a*) Carbon (*b*) Helium
(*c*) Hydrogen (*d*) Neon.

6. Maximum number of electrons that can be accommodated in a 3*d* orbital is
(*a*) Two (*b*) Ten
(*c*) Six (*d*) Fourteen.

7. Which of the following orbitals does not make sense ?
(*a*) 7*s* (*b*) 5*p*
(*c*) 2*d* (*d*) 4*f*.

8. For *ns* orbital, the magnetic quantum number has value
(*a*) 2 (*b*) 4
(*c*) – 1 (*d*) 0.

9. When an electron jumps from a lower energy level to a higher energy level
(*a*) Energy is released (*b*) Energy is absorbed
(*c*) There is no change in energy (*d*) Energy may be absorbed or emitted.

10. The total number of orbitals in an energy level, designated by principal quantum number *n*, is equal to
(*a*) $2n$ (*b*) $2n^2$
(*c*) n (*d*) n^2.

11. The number of *d* electrons in Cr^{3+} ions is
(*a*) 2 (*b*) 3
(*c*) 5 (*d*) 4.

12. The shape of the orbital is determined by the
(*a*) Principal quantum number (*b*) Magnetic quantum number
(*c*) Azimuthal quantum number (*d*) Spin quantum number.

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13. Which of the following quantum numbers does not follow from wave mechanical treatment ?
(a) Principal (b) Magnetic
(c) Spin (d) Azimuthal.

14. A body of mass 100 g is moving with a velocity of 100 ms^{-1}. The wavelength of the de Broglie wave associated with the body would be
(a) 6.62×10^{-34} m (b) 6.62×10^{-38} m
(c) 6.62×10^{-30} m (d) 6.62×10^{-35} m.

15. Which of the following particles having same kinetic energy, would have the maximum de Broglie wavelength ?
(a) Alpha particle (b) Proton
(c) β-particle (d) Neutron.

16. In Ti^{3+}, the number of electrons in the M shell is
(a) 8 (b) 7
(c) 10 (d) 9.

17. In Schrodinger wave equation E represents
(a) Total energy of the electron (b) Potential energy of the electron
(c) Kinetic energy of the electron (d) None of these.

18. The lowest energy level for which *g* subshell is possible is
(a) Fourth (b) Fifth
(c) Sixth (d) Third.

19. The electronic configuration of Fe^{3+} ion is
(a) [Ar] $3d^6$ (b) [Ar] $3d^3, 4s^2$
(c) [Ar] $3d^5$ (d) [Ar] $3d^5, 4s^1$.

20. The two electrons in the *K*-shell will differ in
(a) Principal quantum number (b) Azimuthal quantum number
(c) Magnetic quantum number (d) Spin quantum number.

21. The correct set of quantum numbers for the unpaired electron of chlorine atom is
(a) $n = 2, l = 1, m = 0$ (b) $n = 2, l = 1, m = 1$
(c) $n = 3, l = 1, m = 1$ (d) $n = 3, l = 0, m = 0$.

22. The ground state electronic configuration of copper atom (Z = 29) is
(a) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10}$ (b) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^9 4s^2$
(c) $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^1$ (d) $1s^2 2s^2 2p^6 . 3s^2 3p^6 4s^2 3p^6$.

23. Which of the following sets of quantum numbers is not allowable ?
(a) $n = 3, l = 2, m = 0, s = -\frac{1}{2}$ (b) $n = 3, l = 2, m = -2, s = -\frac{1}{2}$
(c) $n = 3, l = 3, m = -3, s = -\frac{1}{2}$ (d) $n = 3, l = 0, m = 0, s = -\frac{1}{2}$.

24. The correct ground state electronic configuration of chromium atom is
(a) [Ar] $3d^5 4s^1$ (b) [Ar] $3d^4 4s^2$
(c) [Ar] $3d^6 4s^0$ (d) [Ar] $4d^5 4s^1$. *(I.I.T. 1989)*

25. The calculated bond order in H_2^+ ion is
(a) 0 (b) $\frac{1}{2}$
(c) $-\frac{1}{2}$ (d) 1.

26. Out of the following which has smallest bond length ?
(a) O_2 (b) O_2^+
(c) O_2^- (d) O_2^{2-}.

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27. Which of the following species would you predict to be paramagnetic ?

(*a*) O_2^{2+} (*b*) O_2^{2-}

(*c*) H_2 (*d*) H_2^+.

28. Which of the following is paramagnetic ?

(*a*) O_2^- (*b*) CN^-

(*c*) CO (*d*) NO^+. *(I.I.T. 1989)*

29. Which of the following has longest bond length ?

(*a*) O_2 (*b*) O_2^+

(*c*) O_2^- (*d*) O_2^{2-}.

30. Which of the following molecular orbitals in N_2 has least energy ?

(*a*) π_{2p_y} (*b*) σ_{2p_z}

(*c*) σ_{2s} (*d*) $\pi_{2p_x}^*$.

31. Which of the following have identical bond order ?

(*a*) CN^- (*b*) O_2^-

(*c*) NO^+ (*d*) CN^+. *(I.I.T. 1992)*

32. The bond order in N_2^+ ion is

(*a*) 1.5 (*b*) 2.5

(*c*) 2.0 (*d*) 3.0.

33. Which of the following species is diamagnetic ?

(*a*) O_2 (*b*) O_2^+

(*c*) O_2^- (*d*) O_2^{2-}.

34. The molecule which has pyramidal shape is

(*a*) PCl_3 (*b*) SO_3

(*c*) CO_3^{2-} (*d*) NO_3^-. *(I.I.T. 1989)*

35. In sp^3d hybridisation, the *d* orbital that participates in hybridisation is

(*a*) $dx^2 - y^2$ (*b*) dz^2

(*c*) *dxy* (*d*) *dxz*.

36. The orbital angular momentum of electron in 2*s*-orbital is

(*a*) $+\frac{1}{2} \cdot \frac{h}{2\pi}$ (*b*) zero

(*c*) $\frac{h}{2\pi}$ (*d*) $\sqrt{2} \cdot \frac{h}{2\pi}$. *(I.I.T. 1996)*

37. The first use of quantum theory to explain the structure of atom was made by

(*a*) Heisenberg (*b*) Bohr

(*c*) Planck (*d*) Einstein. *(I.I.T. 1997)*

38. Among the following molecules, the one which is polar and has the central atom with sp^2 hybrid state is

(*a*) H_2CO_3 (*b*) SiF_4

(*c*) BF_3 (*d*) $HClO_2$. *(I.I.T. 1997)*

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ASSERTION—REASON TYPE QUESTIONS

The following questions consist of two statements, one labelled as ***Assertion* A** and the other labelled as ***Reason* R**. Examine both the statements and mark the correct choice according to the instructions given below :

(*a*) if both A and R are correct and R is the correct reason of A

(*b*) if both A and R are correct but R is not the correct reason of A

(*c*) A is correct R is wrong

(*d*) A is wrong R is correct.

39. ***Assertion* A :** p_y and p_z cannot combine to give molecular orbital.

***Reason* R :** Both p_y and p_z have dumbell shape.

(*a*) (*b*) (*c*) (*d*)

40. ***Assertion* A :** *s*-orbital cannot accomodate more than two electrons.

***Reason* R :** *s*-orbitals are extremely poor shielders.

(*a*) (*b*) (*c*) (*d*)

41. ***Assertion* A :** When a magnet is dipped in liquid oxygen, some of it sticks to the magnet.

***Reason* R :** Oxygen is paramagnetic in nature.

(*a*) (*b*) (*c*) (*d*)

42. ***Assertion* A :** CO^+ is stabler than CO but NO^+ is less stable than NO.

***Reason* R :** Both CO and NO are gases.

(*a*) (*b*) (*c*) (*d*)

43. ***Assertion* A :** Kinetic energy of photoelectrons is directly proportional to the intensity of the incident radiation.

Rea **:** Each photon of light causes the emission of one photoelectron.

(*a*) (*b*) (*c*) (*d*)

44. ***Assertion* A :** In H atom, the energy of 3*d*-level is smaller than 4*s*-level.

***Reason* R :** An orbital with lower value of $(n + l)$ has energy smaller than the orbital with larger value of $(n + l)$.

(*a*) (*b*) (*c*) (*d*)

45. ***Assertion* A :** 2*p*-orbitals donot have any spherical node.

***Reason* R :** The number of spherical nodes in *p*-orbitals is given by $(n - 2)$, where n is principal quantum number.

(*a*) (*b*) (*c*) (*d*)

FILL IN THE BLANKS

***Fill in the following blanks with some suitable word, formula or a short phrase* :**

1. Metals having low values of ..... are likely to exhibit photoelectric effect.
2. Dual nature of radiations was proposed by .....
3. The wavelength of X-rays is of the order of .....
4. The number of electrons having angular quantum number of 1 and principal quantum number of 2 are .....
5. The orbitals having the equal energies are called .....
6. The energy of electron in second energy level of hydrogen is .....
7. The magnitude of energy of a photon depends upon the ..... of radiation.
8. The lowest energy level in an atom is designated by the letter .....
9. The total number of electrons in a principal energy level is .....

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10. ..... and ..... orbitals have extra stability.
11. Wave nature of electrons is proved by ..... experiment.
12. The number of orbitals in a given energy level is equal to .....
13. Paschen series occur when electron jumps from higher energy levels to ..... energy level.
14. For $l = 2$, the different values of m are .....
15. The molecular orbital formed by addition overlap of $2s$ and $2s$ atomic orbitals is designated as .....
16. O_2^- is ..... stable than O_2.
17. O_2 is ..... because of presence of unpaired electrons.
18. The light radiations with discrete quantities of energy are called ..... *(I.I.T. 1993)*
19. Wave functions of electrons in atoms are called ..... *(I.I.T. 1993)*
20. The $2p_x$, $2p_y$ and $2p_z$ orbitals of atom have identical shapes but differ in their ..... *(I.I.T. 1993)*
21. Out of N_2 and N_2^+, the bond length is shorter in .....
22. Out of N_2, O_2, O_2^{2-} and N_2^+, the paramagnetic species are .....
23. In superoxide ion the number of unpaired electrons is .....
24. In phosphorus pentachloride, PCl_5, the axial bonds have ..... bond length than the equatorial bonds.
25. In IF_7, the iodine atom is ..... hybridised.
26. When N_2 goes to N_2^+, the N—N bond distance ..... but when O_2 goes to O_2^+, the O—O bond distance ..... *(I.I.T. 1996)*
27. Among N_2O, SO_2, I_3^+ and I_3^- the linear species are ..... and ..... *(I.I.T. 1997)*

TRUE/FALSE STATEMENTS

State whether the following statements are True or False :

1. The number of photoelectrons ejected is proportional to the intensity of incident light.
2. Kinetic energy of photoelectrons is proportional to frequency of incident light.
3. All orbitals are spherically symmetrical.
4. A $3d$ sub-shell can accommodate six electrons.
5. The word 'aufbau' in aufbau rule is the name of some scientist.
6. $2p_x$, $2p_y$ and $2p_z$ orbitals are degenerate orbitals.
7. An electron has smaller wavelength than a proton, provided they are moving with same speed.
8. Fourth energy level in He^+ has same energy as the first energy level in hydrogen.
9. In chromium atom there are six electrons in the M-shell.
10. In Mn^{2+} there are five unpaired electrons.
11. The fifth energy level has five subshells.
12. He_2 does not exist because its bond order is zero.
13. N_2^+ is more stable than N_2 whereas O_2^+ is less stable than O_2.
14. N_2^+ has shorter bond length than N_2.
15. O_2^+ has shorter bond length than O_2.

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MATECHING TYPE QUESTIONS

Match the items of Column **A** *with those of Column* **B** :

Column A	Column B
1. $E = hc\bar{v}$	1. Angular momentum of electron in an orbital
2. Occupancy of electrons in degenerate orbitals	2. Pauli's principle
3. 4*d*-orbitals are filled after 5*s*-orbitals	3. Antibonding molecular orbital
4. $\frac{h}{2\pi}\sqrt{l(l+1)}$	4. 3*s*-orbital
5. $\Delta x \cdot \Delta p \approx \frac{h}{4\pi}$	5. Aufbau principle
6. Orbital having 2-spherical nodes.	6. de-Broglie
7. The two electrons in any orbital must have opposite spins :	7. Hund's rule
8. $\psi_{MO} = \psi_A - \psi_B$	8. Energy of a quantum
9. $3s^2\, 3p^6\, 3d^5$	9. Heisenberg's principle
10. $\lambda = \frac{h}{p}$	10. Orbital configuration of Cr^+.

HINTS/ANSWERS

REVIEW PROBLEMS

1.1. 1.99×10^{-18} J
1.2. 4×10^5 J
1.3. 6.25×10^3 Å [**Hint.** 1 eV = 1.6×10^{-19} J]
1.4. $4.8 \times 10^{14}\ s^{-1}$, 6250 Å
1.5. 1.99×10^{-18} J
1.6. 4.02×10^{18} photons
1.7. 3.98×10^{-19} J
1.8. 9 photons
1.9. 1.56×10^{-19} J
1.10. NO, because $\gamma < \gamma$, $\gamma = 5 \times 10^{+14}\ s^{-1}$
1.11. 200 nm
1.12. 1.67×10^{-19} J
1.13. 5.396×10^{-7} m
1.14. 1×10^{16} Hz
1.15. 1200 Å
1.16. 3.3×10^{-24} kg ms^{-1}
1.17. 6.67×10^{-15} m
1.18. 7.94×10^{-38} m
1.19. 6.62×10^{-24} kg ms^{-1}
1.20. $7.3 \times 10^6\ ms^{-1}$
1.21. 7.27×10^{-7} m
1.22. 0.3 Å
1.23. 3.3×10^{-34} m
1.24. 7.25×10^{-7} m
1.25. 1×10^{-10} m
1.26. 7.97×10^{-4} kg ms^{-1}
1.27. $6 \times 10^6\ ms^{-1}$
1.28. $5.77 \times 10^5\ ms^{-1}$
1.29. $2.63 \times 10^{-29}\ ms^{-1}$
1.30. 1.9×10^{-3} m
1.31. $5.8 \times 10^{-5}\ m^2\ s^{-1}$
1.32. 12.3×10^5 J mol^{-1}
1.33. (*a*) 16 ; (*b*) 7

1.34.

Orbital	p_x	p_y	p_z	d_{xy}	d_{yz}	d_z^2	d_{zx}	$d_{x^2-y^2}$
m	+1	−1	0	+2	+1	0	−1	−2

VERY SHORT ANSWER QUESTIONS

1. Metals with low I.E.
2. No. of photoelectrons ∝ intensity of light.
3. Due to light I.E.
4. $n = 3 ; l = 0 ; m = 0 ; s = +\frac{1}{2}$; $n = 3 ; l = 0 ; m = 0 ; s = -\frac{1}{2}$

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5. Yes ; degeneracy is lost. 6. $m = \pm 3, \pm 2, \pm 1, 0$. 8. 3.

9. 2. 10. *Position* and *momentum*.

11. Yes, it is associated with matter waves. As the wavelength of wave is too small to be detected by any physical means, these are of no significance.

12. Orbitals of equal energy ; Five. 13. No, it is in excited state. 14. Infinite.

15. The three $2p$ orbitals differ in orientation. 16. d_{xy} and $d_{x^2-y^2}$.

17. Five. 18. Three. 19. Sixth.

20 Principal quantum number – size,
Azimuthal quantum number – shape.

21. $3f$ and $2d$. 22. 0, 1, 2 and 3. 23. 18.

24. + 3, + 2, + 1, 0, – 1, – 2, – 3. 25. $n = 3, l = 0, m = +1, 0, -1$.

26. Na : $1s^2, 2s^2, 2p^6, 3s^1$
$n = 3, l = 0, m = 0, s = +1/2$ or $-1/2$.

27. $3p$ orbital has higher energy than $2p$. $3p$ orbital has a spherical node whereas $2p$ has no spherical node.

28. Yes, these are two unpaired electrons ($\pi^1{}_{2p_x}, \pi^1{}_{2p_y}$).

29. $F_2 > O_2 > N_2$. 30. $d_{z^2}, d_{x^2-y^2}$.

31. It is because of intermixing of energies of $2s$ and $2p$-orbitals due to close proximity.

32. H_2^+ ; It is because electron in H_2^+ is present only in bonding orbital.

33. Two ; $d_{x^2-y^2}$ and d_{xy}. 35. Bond order = 1/2. 36. Bond order = 3.

38. Azimuthal quantum number (or angular momentum quantum number), l.

40. In the shell with $n = 4$, the possible values of l are 0, 1, 2 and 3. The corresponding subshells are :
$4s, 4p, 4d$ and $4f$.

41. sp^2. 43. sp^2. 44. + 1, 0, – 1.

DESCRIPTIVE QUESTIONS

52. $E = \frac{hc}{\lambda}, E \propto \frac{1}{\lambda}$. 53. K.E. ∝ Frequency of the incident radiation.

64. $\lambda = \frac{h}{mc}$. 66. (*i*) Principal quantum number ; (*ii*) Azimuthal quantum number.

67. $E_n \propto \frac{1}{n^2}$; $E_n = k^2 \frac{2\pi^2 me^4}{n^2h^2}$. 68. For N-shell $n = 4$ $\therefore$ $l = 0, 1, 2, 3$.

69. + 2. 71. By specifying quantum numbers n, l and m.

72. $l = 2$; $m = +2, +1, 0, -1, -2$. 73. $2p_x : n = 2, l = 1, m = +1$; $3p_z : n = 3, l = 1, m = 0$.

75. No, because when $n = 3$, l can have values 0, 1 and 2 and not 3.

76. The valence shell electrons in N are $2s^2, 2p_x^1, 2p_y^1, 2p_z^1$

$$2s^2 \left[\begin{array}{llll} n=2, & l=0, & m=0, & s=+\frac{1}{2} \\ n=2, & l=0, & m=0, & s=-\frac{1}{2} \end{array} \right. \qquad 2p^3 \left[\begin{array}{llll} n=3, & l=1, & m=+1, & s=+\frac{1}{2} \\ n=3, & l=1, & m=0, & s=+\frac{1}{2} \\ n=3, & l=1, & m=-1, & s=+\frac{1}{2} \end{array} \right.$$

78. (*i*) It is not allowed because when $l = 2$, m cannot be + 3
(*ii*) It is not allowed because l cannot be 4 when $n = 4$. l cannot be numerically equal to n
(*iii*) This set is not permitted because n cannot be zero

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(*iv*) This set is allowed

(*v*) This set is not allowed because s cannot be $-3/2$.

79. (*i*) 18 (*ii*) 10 (*iii*) 2.

80. (*i*) 16 (*ii*) 7.

82. $3s$ has two spherical nodes, $2s$ orbital is of larger size and has a spherical node.

83. (*i*) 18 (*ii*) 6 (*iii*) 2.

84. Orbitals having equal energy are called degenerate orbitals. For example, $2p_x$, $2p_y$ and $2p_z$ orbitals are degenerate.

85. (*i*) $4s = 4p = 4d = 4f$ (*ii*) $4s < 4p > 4d > 4f$.

97. (*i*) 5, (*ii*) 9, (*iii*) 3, (*iv*) 9, (*v*) 6.

98. Fe^{2+} : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^6$

Fe^{3+} : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^5$

Cr^{3+} : $1s^2, 2s^2, 2p^6, 3s^2, 3p^6, 3d^3$

Fe^{3+} has maximum number of unpaired electrons.

117. Yes, there are two unpaired electrons in B_2.

118. $F_2 > O_2 > N_2$. **119.** d_{z^2} and $d_{x^2-y^2}$.

120. It is because of intermixing of energies of $2s$ and $2p$ orbitals due to close proximity.

121. H_2^+ is more stable than H_2^- because in H_2^+ the electron is present only in bonding orbital.

122. 1/2. **123.** 3.

133.
$$\text{K.E.} = hc\left[\frac{1}{\lambda} - \frac{1}{\lambda^\circ}\right]$$
$$= 6.62 \times 10^{-34} \times 3 \times 10^8 \left[\frac{1}{220 \times 10^{-9}} - \frac{1}{260 \times 10^{-9}}\right]$$
$$= \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{10^{-9}}\left[\frac{1}{220} - \frac{1}{260}\right] = \mathbf{1.39 \times 10^{-19}\ J.}$$

134. Distance = 300 Km = 300×10^3 m

Velocity = 3×10^8 m s^{-1}

$$\text{Time} = \frac{\text{Distance}}{\text{Velocity}} = \frac{300 \times 10^3}{3 \times 10^8 \text{ m s}^{-1}} = \mathbf{1 \times 10^{-3}\ s.}$$

135. Energy of one photon, $E = h\nu = \frac{hc}{\lambda} = \frac{6.62 \times 10^{-34} \times 3 \times 10^8}{300 \times 10^{-9}} = 6.62 \times 10^{-19}$ J

Energy of one mole photons = $6.62 \times 10^{-19} \times 6.02 \times 10^{23} = \mathbf{3.98 \times 10^5\ J.}$

136. $E = h\nu = 6.62 \times 10^{-34} \times 1 \times 10^{15} = 6.62 \times 10^{-19}$ J

$$\text{Number of photons} = \frac{\text{Energy needed}}{\text{Energy per photon}} = \frac{1 \times 10^3 \text{ J}}{6.62 \times 10^{-19} \text{ J/photon}} = \mathbf{1.51 \times 10^{21}\ photons.}$$

137. $\lambda = \frac{h}{mc}$

$$m = \frac{h}{c\lambda} = \frac{6.62 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{3 \times 10^8 \text{ m s}^{-1} \times 600 \times 10^{-9} \text{ m}} = \mathbf{3.68 \times 10^{-36}\ kg.}$$

138. $\lambda_A = \frac{h}{p_A}$, $\lambda_B = \frac{h}{p_B}$

$$\frac{\lambda_A}{\lambda_B} = \frac{p_B}{p_A} = \frac{1/2\, p_A}{p_A} = \frac{1}{2} \qquad \frac{5 \times 10^{-8} \text{ m}}{\lambda_B} = \frac{1}{2}, \lambda_B = 2 \times 5 \times 10^{-8} \text{ m} = \mathbf{1 \times 10^{-7}\ m.}$$

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139. $m = 1000$ kg

$v = 300$ km/hr

$= \frac{300 \times 1000}{3600}$ m/s

$\lambda = \frac{h}{mv} = \frac{6.625 \times 10^{-34} \times 3600}{1000 \times 300 \times 1000} = \mathbf{7.95 \times 10^{-39}}$ **m.**

140. Velocity of electrons, $v = 3 \times 10^8 \times \frac{1}{100} = 3 \times 10^6$ m s^{-1}

Mass of electron, $m = 9.1 \times 10^{-31}$ kg

$$\lambda = \frac{h}{mv} = \frac{6.22 \times 10^{-34}}{9.1 \times 10^{-31} \times 3 \times 10^6} = \mathbf{2.42 \times 10^{-10}} \text{ m.}$$

141. $\lambda = 0.1$ nm $= 0.1 \times 10^{-9}$ m $= 1.0 \times 10^{-8}$ m

$\lambda = \frac{h}{p}$

$p = \frac{h}{\lambda} = \frac{6.6 \times 10^{-34}}{1.0 \times 10^{-8}} = \mathbf{6.6 \times 10^{-26}}$ **kg m s^{-1}**

142. $\Delta x \,.\, m\Delta v = \frac{h}{4\pi}$

$\Delta x \,.\, \Delta v = \frac{h}{4\pi m} = \frac{6.62 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{4 \times 22/7 \times 9.1 \times 10^{-31} \text{ kg}} = \mathbf{5.78 \times 10^{-5}}$ **m^2 s^{-1}.**

143. $\Delta x = 10^{-5}$ m

$m = 10$ g $= 0.01$ kg

$\Delta x \,.\, m\Delta v = \frac{h}{4\pi}$

$$\Delta v = \frac{h}{4\pi m \,.\, \Delta x} = \frac{6.62 \times 10^{-34} \text{ kg m}^2\text{s}^{-1}}{4 \times 22/7 \times 0.01 \text{ kg} \times 10^{-5} \text{ m}} = \mathbf{5.26 \times 10^{-28}} \text{ ms}^{-1}.$$

MULTIPLE CHOICE QUESTIONS

1. (*c*)	**2.** (*c*)	**3.** (*b*)	**4.** (*d*)	**5.** (*c*)	**6.** (*a*)
7. (*c*)	**8.** (*d*)	**9.** (*b*)	**10.** (*d*)	**11.** (*b*)	**12.** (*c*)
13. (*c*)	**14.** (*d*)	**15.** (*c*)	**16.** (*d*)	**17.** (*a*)	**18.** (*b*)
19. (*c*)	**20.** (*d*)	**21.** (*c*)	**22.** (*c*)	**23.** (*c*)	**24.** (*a*)
25. (*b*)	**26.** (*b*)	**27.** (*d*)	**28.** (*a*)	**29.** (*d*)	**30.** (*c*)
31. (*a*), (*c*)	**32.** (*b*)	**33.** (*d*)	**34.** (*a*)	**35.** (*b*)	**36.** (*b*)
37. (*b*)	**38.** (*d*)	**39.** (*b*)	**40.** (*b*)	**41.** (*a*)	**42.** (*b*)
43. (*d*)	**44.** (*b*)	**45.** (*a*).			

FILL IN THE BLANKS

1. ionisation energy	**2.** Einstein	**3.** 1 Å
4. 6	**5.** degenerate orbitals	**6.** – 328 kJ/mole
7. frequency	**8.** K	**9.** $2n^2$
10. fully-filled, half-filled	**11.** diffraction	**12.** n^2
13. third	**14.** + 2, + 1, 0, – 1, – 2	**15.** σ_{2s}

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16. less
17. paramagnetic
18. Photons
19. atomic orbitals or simply orbitals
20. orientation
21. N_2
22. O_2 and N_2^+
23. 1
24. longer or greater
25. sp^3d^3
26. increases, decreases
27. N_2O and I_3^-.

TRUE/FLASE STATEMENTS

1. True
2. True
3. False
4. False
5. False
6. True
7. False
8. False
9. False
10. True
11. True
12. True
13. False
14. False
15. True.

MATCHING TYPE QUESTIONS

1—8 ; 2—7 ; 3—5 ; 4—1 ; 5—9 ;
6—4 ; 7—2 ; 8—3 ; 9—10 ; 10—6.

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2

The Solid State

LEARNING OBJECTIVES

In this Unit, we shall learn

- *structures of simple ionic compounds* ;
- *structures of substances explained by the close-packed structure, silicates* ;
- *ionic radii* ;
- *electronic and atomic imperfections in solids* ;
- *properties of crystalline solids including magnetism and superconductivity* ;
- *some features of amorphous solids.*

In the previous class, we studied about the characteristics and classification of crystalline solids. We also studied ~~the close~~ packing of spheres. The arrangement of atoms of most of the metals takes place in a similar way. In this unit, we shall discuss structures of some simple ionic solids. We shall also study about structure of silicates and amorphous solids. Since in compounds also, the packing of constituent particles tends to be as economical as possible therefore before we discuss structures of compounds let us review what we had studied in class XI about the crystal lattices and close packing of spheres.

2.1. SPACE LATTICE OR CRYSTAL LATTICE

A crystal can be imagined to be generated from the repetition of some basic unit of pattern such as atom, molecule, ion or a group of ions. While representing the relative arrangement of these units in a crystal, it is much more convenient to represent each unit of pattern by a point, called lattice point, rather than drawing the entire unit of pattern. This results in a three dimensional orderly arrangement of points called a space lattice or a crystal lattice. Thus, **a space lattice may be defined as a regular three dimensional arrangement of identical points in space.**

An example of space lattice has been shown in Fig. 2.1.

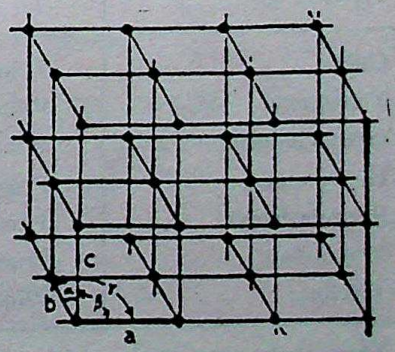

Fig. 2.1. A crystal lattice. The shaded portion represents the unit cell.

It must be noted here that,

(*i*) each lattice point has the same environment as that of any other point in the lattice.

(*ii*) The constituent particle has always to be represented by a lattice point, irrespective of whether it contains a single atom or more than one atoms.

2.2. UNIT CELLS

For every crystal lattice it is possible to select a group of lattice points which is repeated again and again. This part of the space lattice is called unit cell. The entire lattice can be generated by translation or stacking of these unit cells. Thus, **a unit cell may be defined as a three dimensional group of lattice points that generates the whole lattice by translation or stacking.**

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Types of Unit Cells

(*i*) *A unit cell having lattice points only at the corners* is called **simple, primitive or basic unit cell.** A crystal lattice having primitive unit cell is called **simple crystal lattice.**

(*ii*) *A unit cell having lattice points at the centre of each face, in addition to the lattice points at the corners* is called **face centred unit cell.**

(*iii*) *A unit cell having a lattice point at the centre of the body, in addition to the lattice points at the corners,* is called **body centred unit cell.**

The three types of cubic unit cells are illustrated in Fig. 2.2.

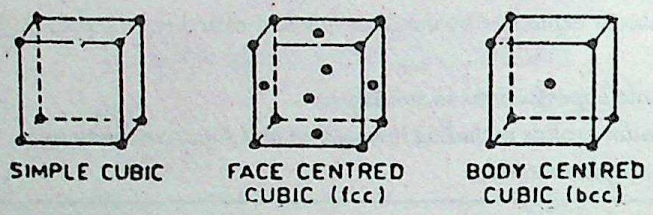

Fig. 2.2. Types of cubic unit cells.

It may be mentioned here that another type of unit cell, called end centred unit cell, is possible for orthorhombic and monoclinic crystal types.

In an ***end centred unit cell,*** *there are lattice points in the face centres of only one set of faces, in addition to the lattice points at the corners of the unit cell.*

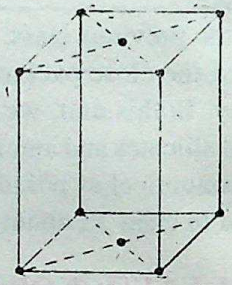

Fig. 2.2. (*a*) An end centred unit cell.

It may be noted that all the four types of unit cells are not possible for each crystal class.

The various types of unit cells possible for different crystal classes are given below in tabular form :

Crystal class	*Possible types of unit cells*
Cubic	Primitive, Body centred, Face centred
Tetragonal	Primitive, Body centred
Orthorhombic	Primitive, Body centred, Face centred, End centred
Hexagonal	Primitive
Rhombohedral	Primitive
Monoclinic	Primitive and End centred
Triclinic	Primitive

Thus, there are seven crystal types for which fourteen different types of lattices (7 primitive, 3 body centred, 2 face centred and 2 end centred) are possible. These fourteen different types of lattices are known as **Bravais lattices.**

Calculation of Number of Particles in a Unit Cell

In order to calculate the number of particles in a unit cell, the following rules must be obeyed :

1. Each particle at the corner of a unit cell is shared by eight unit cells in the lattice and hence contributes only $\frac{1}{8}$ to a particular unit cell.
2. A particle at the edge centre is shared by four unit cells in the lattice and hence contributes only $\frac{1}{4}$ to a particular unit cell.

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3. A particle at the centre of the face of a unit cell is shared by two unit cells in the lattice and contributes only $\frac{1}{2}$ to a particular unit cell.

4. A particle at the body centre of a unit cell belongs only to the particular unit cell.

Now, by applying these rules, let us calculate the number of atoms in the different cubic unit cells of monoatomic substances.

Simple cubic. In this type of unit cell, there are eight atoms at the corners (Fig. 2.2) and each such atom makes $\frac{1}{8}$ contribution to the unit cell. Hence, *a simple cubic unit cells has*

$$8 \text{ (at corners)} \times \frac{1}{8} = 1 \text{ atom.}$$

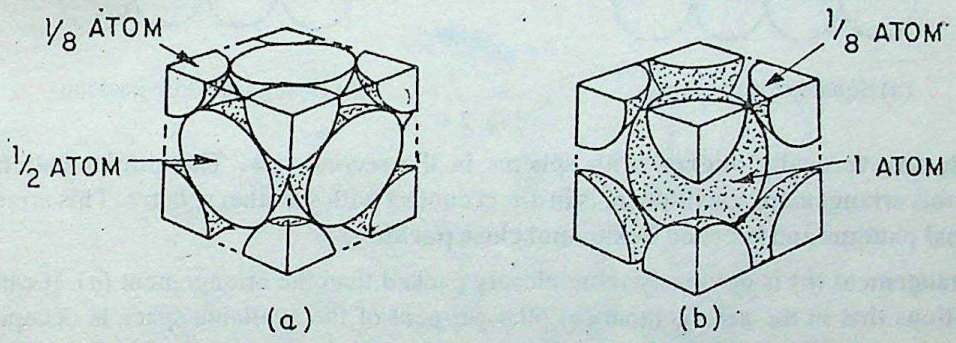

Fig. 2.3. (*a*) Three-dimensional view showing four atoms per unit cell in case of cubic close-packed structure. (*b*) Three-dimensional view showing two atoms per unit cell in a body-centred cubic structure.

Body centred cubic. This type of unit cell has eight atoms at corners and one at the body centre. Each corner atom makes $\frac{1}{8}$ contribution and the atom at the body centre belongs only to the particular unit cell. Hence, *a body centred cubic unit cell has*

$$8 \text{ (at corners)} \times \frac{1}{8} + 1 \text{ (at body centre)} \times 1 = 2 \text{ atoms.}$$

Face centred cubic. A face centred cubic unit cell has one atom at each corner (there are eight corners of a cube) and one atom at each face centre (there are six faces of a cube). An atom at the face centre is being shared by two unit cells and makes a contribution of only $\frac{1}{2}$ to a particular unit cell. Hence, *a face centred cubic unit cell has*

$$8 \text{ (at corners)} \times \frac{1}{8} + 6 \text{ (at face centres)} \times \frac{1}{2} = 4 \text{ atoms.}$$

2.3. PACKING OF CONSTITUENTS IN CRYSTALS

In the formation of crystals the constituent particles try to pack as closely as possible so as to attain a state of maximum possible density and stability. Since in different crystals, the units of pattern have different shapes and sizes, the actual mode of closest packing is different for different crystals. In this section, we shall focus on close packing modes of spherical particles of equal size. In metallic crystals the constituent particles are nearly of this type.

Close Packing in Two Dimensions

In order to understand the close packing of spheres, first of all, let us consider how the spheres can be arranged in a plane. The two possible arrangements are shown in Fig. 2.4. In the arrangement (*a*) the spheres in the adjacent rows lie just one over the other and show a horizontal as well as vertical alignment, and form

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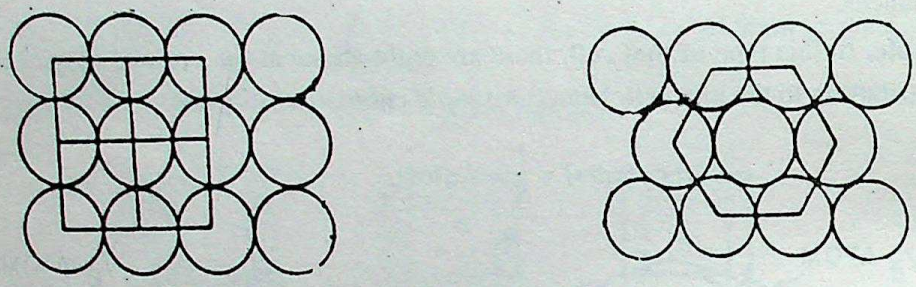
squares. This type of packing is called **square close packing.** Each sphere in this arrangement is in contact with four other spheres.

In the arrangement (*b*), the spheres in every second row are seated in the depressions between the spheres of the first row. The spheres in the third row are vertically aligned with the spheres in the first row and



(*a*) Square close packing. (*b*) Hexagonal close packing.

Fig. 2.4

those in fourth row vertically aligned with spheres in the second row. The similar pattern is followed throughout. In this arrangement, each sphere is in direct contact with six other spheres. This arrangement gives rise to hexagonal patterns and is called **hexagonal close packing.**

The arrangement (*b*) is obviously more closely packed than the arrangement (*a*). It can be shown by simple calculations that in the arrangement (*b*) 60.4 per cent of the available space is occupied by spheres whereas in arrangement (*a*) only 52.4 per cent of the space is occupied by spheres. If only one layer of spheres is to be packed, the spheres will arrange themselves according to hexagonal close packing because it is more efficient. In this arrangement there are a number of vacant spaces or voids. These vacant spaces are between three touching spheres whose centres lie at the corners of an equilateral triangle. These vacant spaces are, therefore, called **triangular voids.**

Close Packing in Three Dimensions

In order to develop three dimensional close packing, let us retain the hexagonal close packing in the first layer because it is the most efficient. If the spheres in the second layer are just placed over the spheres in the first layer so that the spheres in the two layers are vertically aligned then the voids in the two layers will also cover each other. This will amount to an inefficient filling of space. For close packing each sphere in the second layer rests in the hollow at the centre of three touching spheres in the layer as shown in Fig. 2.5 (*b*). The spheres in the first layer are shown by solid lines while those in second layer are shown by broken lines. It may be noted that only half the triangular voids in the first layer are occupied by spheres in the second layer (*i.e.*, either *b* or *c*). The unoccupied hollows or voids in the first layer are indicated by (*c*) in Fig. 2.5.

There are two alternative ways in which spheres in the third layer can be arranged over the second layer. The third layer can lie vertically above the first if the spheres in the third layer rest in one set of hollows [corresponding to centres of the spheres (marked by *a*) in the first layer] on the top of the second layer, alternatively, the third layer can be different from the first if the spheres in the third layer lie on the other set of hollows which correspond to those marked '*c*' in the first layer. The first arrangement is called ABAB... type while the second alternative is called ABC ABC... type. These two arrangements are equally efficient. In either type of close packing 74.0 per cent of the available space is occupied by spheres. They differ from each other in overall symmetry. *The AB AB... arrangement has hexagonal symmetry and is known as* **hexagonal close packing (hcp)** (Fig. 2.6). *The ABC ABC... packing has cubic symmetry and is known as* **cubic close packing (ccp)** (Fig. 2.7). The cubic close packing has *face centred cubic* (fcc) unit cell.

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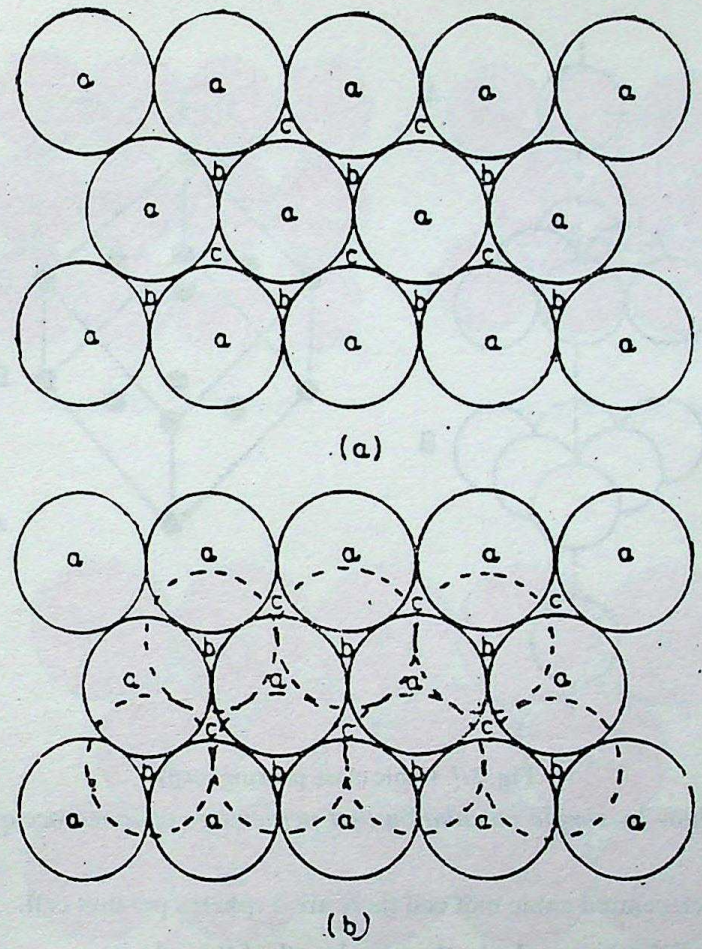

Fig. 2.5. Close packing of spheres

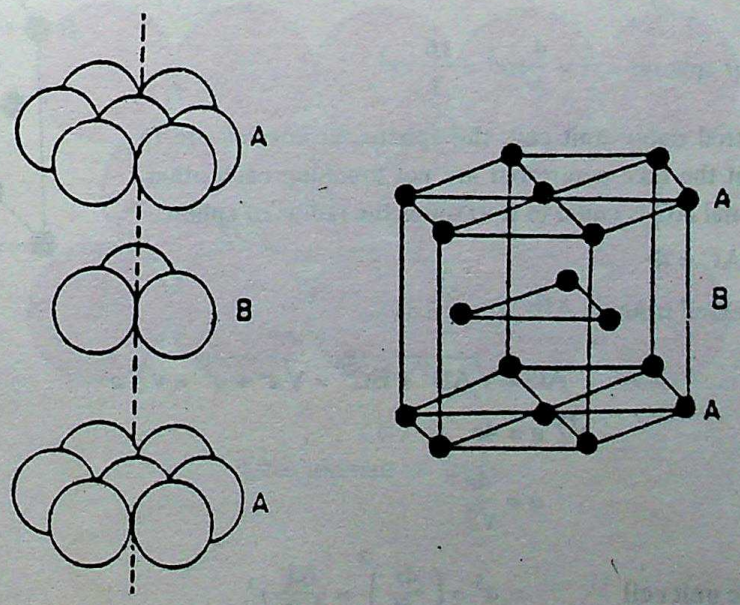

Fig. 2.6. Hexagonal close packing (hcp).

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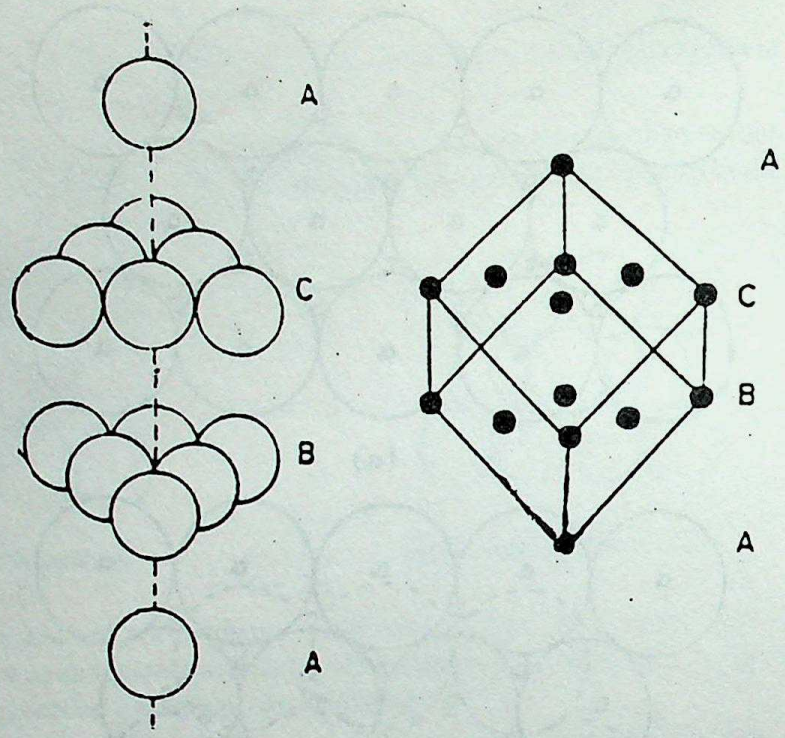

Fig. 2.7. Cubic close packing (ccp).

Example 2.1. *Show by simple calculation that percentage of space occupied by spheres in a face centred unit cell is 74%.*

Solution. In a face centred cubic unit cell there are 4 spheres per unit cell.

Let r be the radius of sphere and a be the edge length of the cube.

Volume of sphere $= \frac{4}{3}\pi r^3$

Volume of four spheres $= 4 \times \frac{4}{3}\pi r^3 = \frac{16}{3}\pi r^3$

In a face centred cubic unit cell, the spheres at corners are in contact with sphere at the face centre but are not touching each other. Therefore, face diagonal AC is equal to four times the radius of sphere.

$$AC = 4r$$

But in right angled triangle ABC (Fig. 2.8)

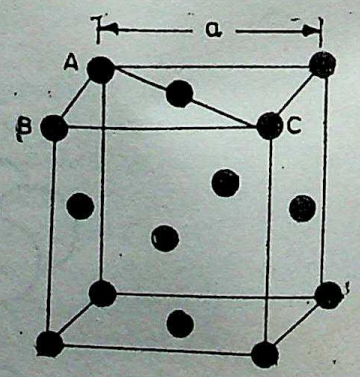

Fig. 2.8

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}\, a$$

$$\therefore \quad \sqrt{2}\, a = 4r$$

$$a = \frac{4r}{\sqrt{2}}$$

Volume of the unit cell $= a^3 = \left(\frac{4r}{\sqrt{2}}\right)^3 = \frac{64}{2\sqrt{2}} r^3.$

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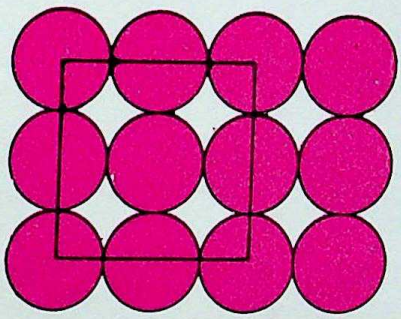
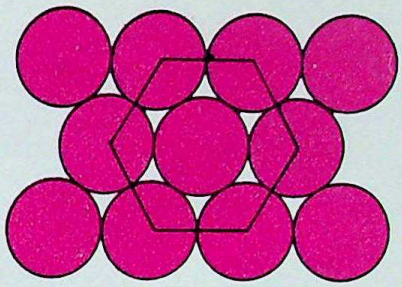
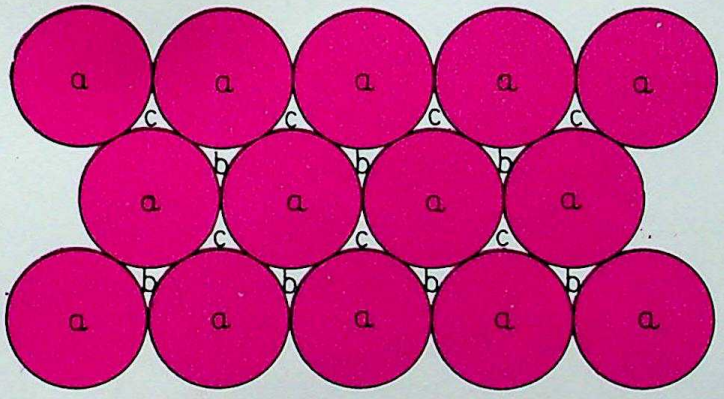


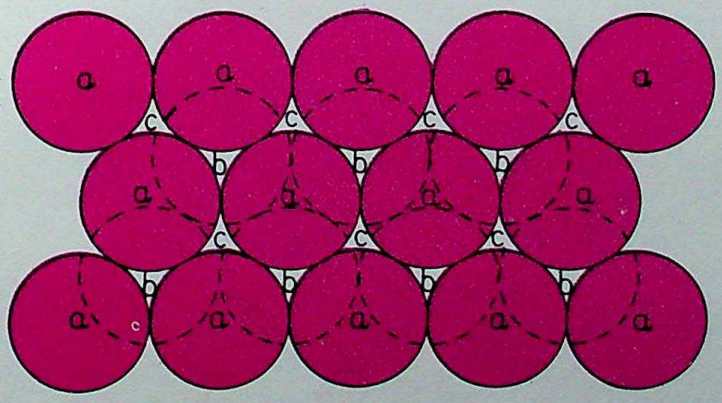
SQUARE CLOSE PACKING



HEXAGONAL CLOSE PACKING



(a)



(b)

CLOSE PACKING OF SPHERES

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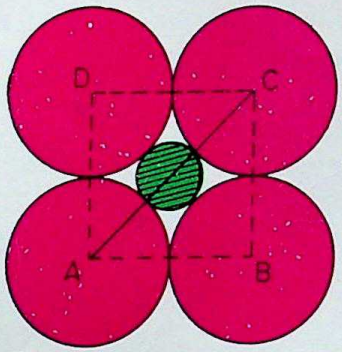
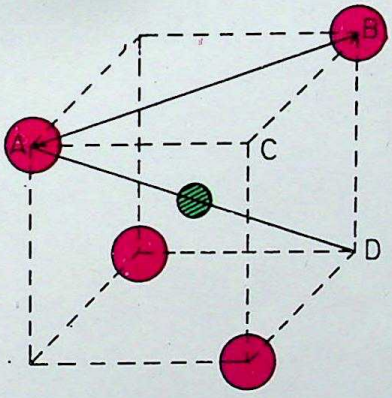
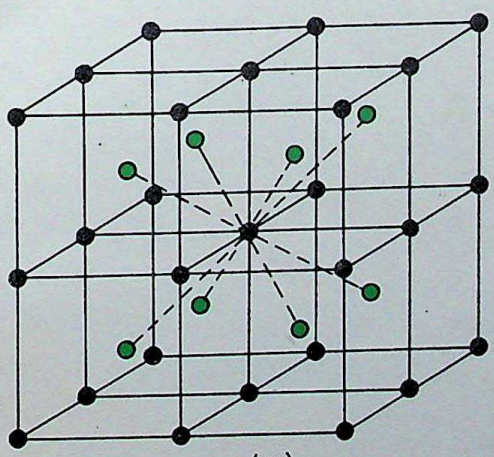


OCTAHEDRAL VOID

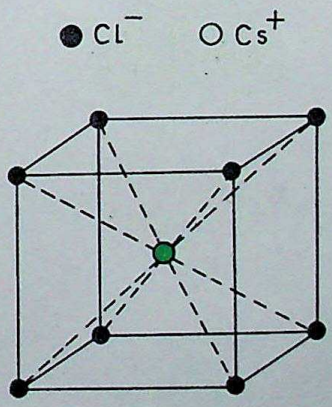


TETRAHEDRAL VOID



(a)

CsCl LATTICE



(b)

CsCl UNIT CELL

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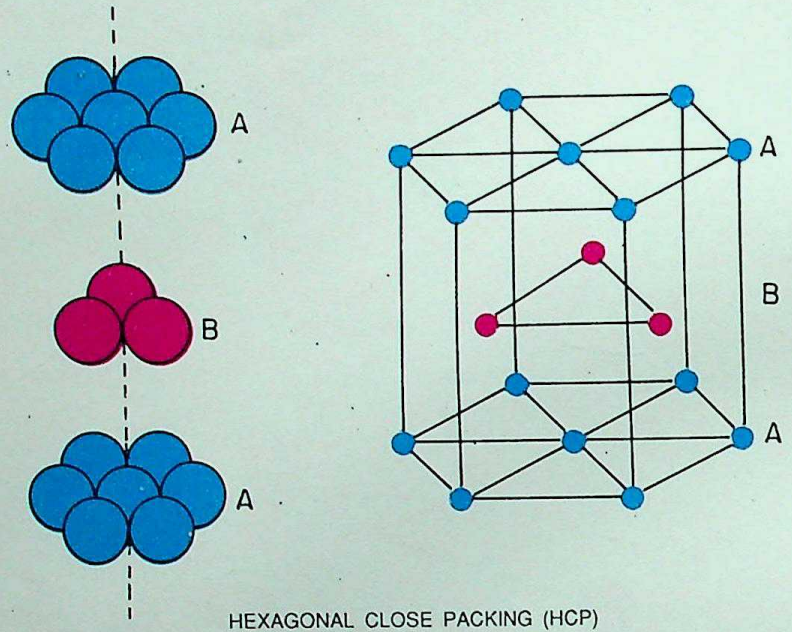
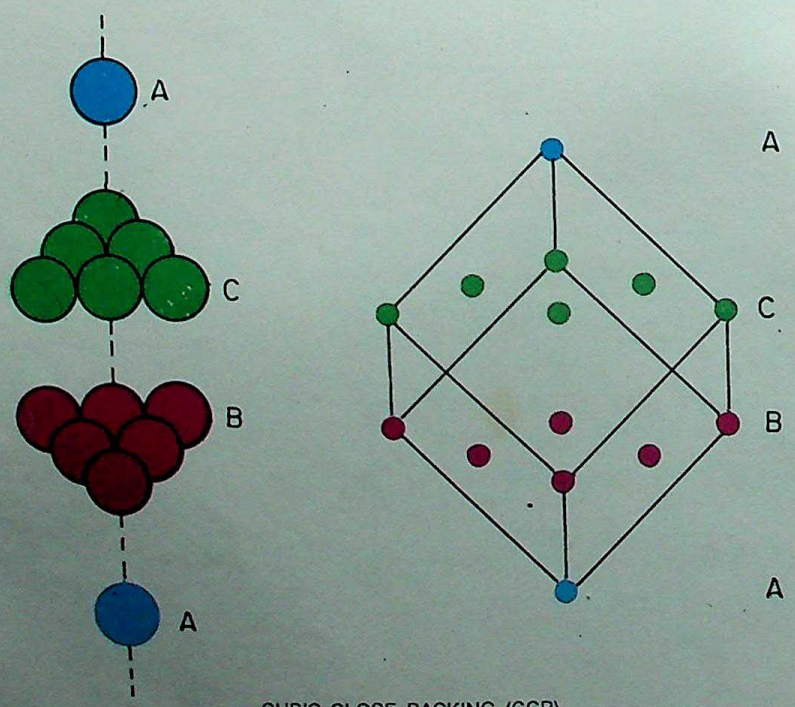


HEXAGONAL CLOSE PACKING (HCP)



CUBIC CLOSE PACKING (CCP)

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Percentage of space occupied by spheres

$$= \frac{\text{Volume of spheres}}{\text{Volume of cube}} \times 100$$

$$= \frac{\frac{16}{3}\pi r^3}{\frac{64}{2\sqrt{2}} r^3} \times 100 = \frac{16}{3} \times \frac{22}{7} \times \frac{2\sqrt{2}}{64} \times 100 = \mathbf{74\%}.$$

OPEN STRUCTURES

In both the *hcp* and *fcc* arrangements 74% of the available space is occupied by spheres. Another arrangement in which the packing is not quite so close is also found in case of many solids. This arrangement is **body centred cubic (bcc)** arrangement. In this arrangement only **68%** of the available space is occupied by spheres. A *bcc* unit cell is shown below in Fig. 2.9.

Percentage of Space occupied by Spheres (atoms) in a Body Centred Cubic Unit Cell

We know that in a body centred cubic unit cell there are two spheres per unit cell. Let a be the side of the unit cell and r be the radius of sphere.

Volume of sphere $= \frac{4}{3}\pi r^3$

Volume occupied by two spheres $= 2 \times \frac{4}{3}\pi r^3 = \frac{8}{3}\pi r^3$

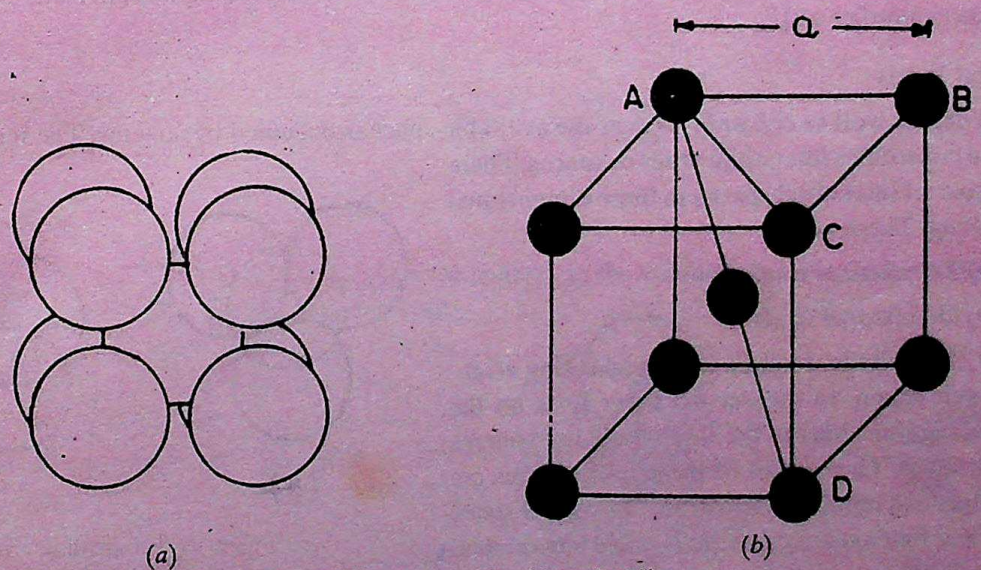

Fig. 2.9. Body centred cubic unit cell.

In right angled triangle ABC [Fig. 2.9 (*b*)]

Face diagonal $AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2a^2}\, a = \sqrt{2}a$

In right angled triangle ACD

Body diagonal $AD = \sqrt{AC^2 + CD^2} = \sqrt{2a^2 + a^2} = \sqrt{3}a$

In a body centred cubic unit cell, the spheres at the corners are not touching each other but are in contact with the sphere at the centre. As a result the body diagonal AD is equal to the four times the radius of the sphere.

$$\therefore \quad AD = \sqrt{3}a = 4r$$

$$a = \frac{4}{\sqrt{3}} r$$

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Volume of unit cell $= a^3 = \left(\frac{4}{\sqrt{3}} r\right)^3 = \frac{64}{3\sqrt{3}} r^3$

Percentage of space occupied by spheres $= \frac{\text{Volume of spheres}}{\text{Volume of cube}} \times 100$

$$= \frac{\frac{8}{3}\pi r^3}{\frac{64}{3\sqrt{3}} r^3} \times 100 = \frac{8}{3} \times \frac{22}{7} \times \frac{3\sqrt{3}}{64} \times 100 = \mathbf{68\%}.$$

Some examples of metallic solids having *hcp*, *fcc* and *bcc* arrangements are given below :

Hexagonal Close Packed	Magnesium, Zinc, Cadmium and Titanium
Face Centred Cubic	Nickel, Copper, Silver, Gold and Aluminium
Body Centred Cubic	Sodium, Potassium, Rubidium, Tungsten, Chromium and Iron

Co-ordination Number

In the two types of three dimensional close packing (hcp and ccp) discussed above, each sphere is touching six other spheres in its own layer, three spheres in the layer above and three spheres in the layer below. Thus, in a close packing arrangement a sphere is touching 12 other spheres. *The number of nearest neighbours in a packing is called* **co-ordination number**. In close packing arrangement each sphere has a co-ordination number of 12.

Interstitial Voids

In *hcp* as well as *ccp* only 74% of the available space is occupied by spheres. The remaining space is vacant and constitutes interstitial voids or spaces. There are two types of interstitial spaces in three dimensional close packing. These are :

(*a*) *Tetrahedral voids*

(*b*) *Octahedral voids.*

(*a*) **Tetrahedral voids.** In close packing arrangement each sphere in the second layer rests on the hollow (triangular void) in the three touching spheres in the first layer. The centres of these four spheres are at the corners of a regular tetrahedron. *The vacant space between these four touching spheres* is called **tetrahedral void** (Fig. 2.10).

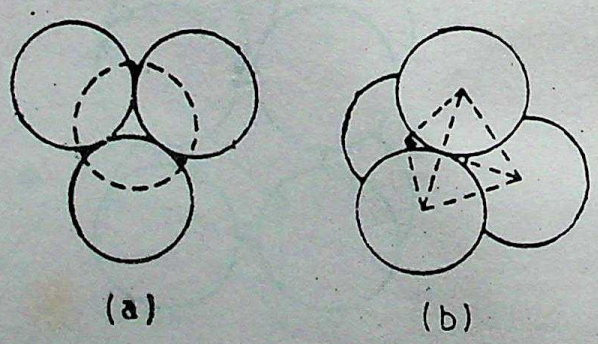

Fig. 2.10. Tetrahedral void.

In a close packing, the number of tetrahedral voids is double the number of spheres. So there are two tetrahedral voids associated with each sphere, one above the sphere and one below the sphere. Radius of the tetrahedral void relative to the radius of the sphere is 0.225, *i.e.*, for tetrahedral void

$$\frac{r_{void}}{r_{sphere}} = 0.225.$$

Radius ratio of tetrahedral void

A tetrahedral site in a cube is shown in Fig. 2.11. Here the shaded sphere represents the tetrahedral void. Now if we assume that the face length of the cube = a and r_1 and r_2 are the radii of the void and the sphere respectively then considering the right angled triangle ABC.

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Face diagonal, $AB = \sqrt{AC^2 + BC^2} = \sqrt{a^2 + a^2}$

$= \sqrt{2}\, a$

or $2r_2 = \sqrt{2}\, a$

[∵ Along length AB, the two spheres with radius r_2 touch each other.

∴ $AB = r_2 + r_2 = 2r_2$]

or $r_2 = \frac{\sqrt{2}}{2} a = \frac{1}{\sqrt{2}} a$ ...(*i*)

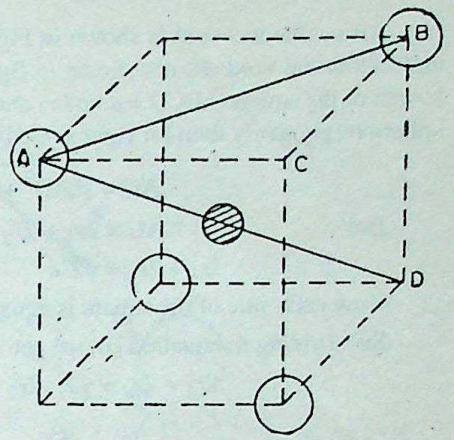

Fig. 2.11

Similarly, considering the right angled triangle ABD, the body diagonal AD is given as

$$AD = \sqrt{AB^2 + BD^2}$$

$$= \sqrt{(\sqrt{2}\, a)^2 + a^2} = \sqrt{3}\, a$$

or $2r_1 + 2r_2 = \sqrt{3}\, a$ [∵ length $AD = 2r_1 + 2r_2$]

or $r_1 + r_2 = \frac{\sqrt{3}}{2} a$ ...(*ii*)

Dividing eqn. (*ii*) by eqn. (*i*), we get

$$\frac{r_1 + r_2}{r_2} = \frac{\sqrt{3}}{2} a \cdot \frac{\sqrt{2}}{a} = \frac{\sqrt{3}}{\sqrt{2}}$$

or $\frac{r_1}{r_2} + 1 = \frac{\sqrt{3}}{\sqrt{2}}$

or $\frac{r_1}{r_2} = \frac{\sqrt{3}}{\sqrt{2}} - 1 = \frac{\sqrt{3} - \sqrt{2}}{\sqrt{2}} = \frac{1.732 - 1.414}{1.414} = \mathbf{0.225.}$

Thus, for a tetrahedral void $\frac{r_{void}}{r_{sphere}} = 0.225.$

(*b*) **Octahedral voids.** As already discussed the spheres in the second layer rest on the triangular voids in the first layer. However, one half the triangular voids in the first layer are occupied by the spheres in the second layer while the other half marked '*c*' (Fig. 2.5) remain unoccupied. The triangular voids '*c*' in the first layer are overlapped by the triangular voids in the second layer. *The interstitial void formed by combination of two triangular voids of the first and second layer* is called **octahedral void** because this is enclosed between six spheres, centres of which occupy corners of a regular octahedron. The octahedral void is shown in Fig. 2.12.

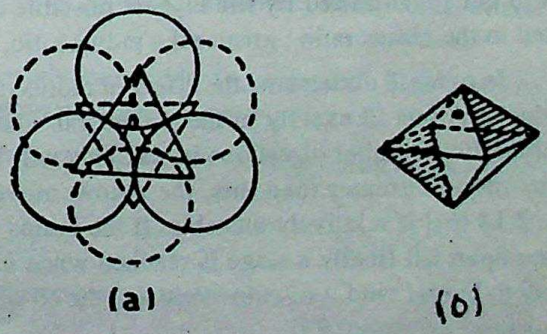

Fig. 2.12. Octahedral void.

In a close packing, the number of octahedral voids is equal to the number of spheres. Thus, there is only one octahedral void associated with each sphere. Radius of the octahedral void relative to the radius of the sphere is 0.414, *i.e.*, for octahedral void.

$$\frac{r_{void}}{r_{sphere}} = 0.414.$$

Octahedral void is larger than a tetrahedral void :

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Radius ratio of Octahedral void

An octahedral void is shown in Fig. 2.13. The spheres present above and below the void are not shown in figure. Now, if we assume that each length of the square ABCD = a and r_1 and r_2 are the radii of the void and the sphere respectively then for right angled triangle ABC

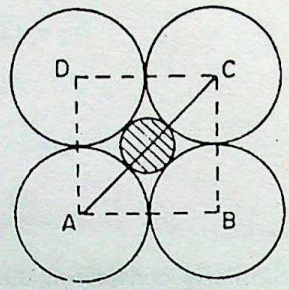

Fig. 2.13

$$AC = \sqrt{AB^2 + BC^2} = \sqrt{a^2 + a^2} = \sqrt{2}\, a$$

But $\quad AC = 2r_1 + 2r_2$

$\therefore \quad 2r_1 + 2r_2 = \sqrt{2}\, a \qquad ...(i)$

Now each side of the square is equal to $2r_2$, *i.e.*, $a = 2r_2$

Substituting in equation (i), we get

$$\therefore \quad 2r_1 + 2r_2 = \sqrt{2} \,.\, 2r_2$$

$$\frac{r_1}{r_2} + 1 = \sqrt{2}$$

$$\frac{r_1}{r_2} = \sqrt{2} - 1 = 1.414 - 1 = \mathbf{0.414.}$$

Thus, for an octahedral void, $\dfrac{r_{void}}{r_{sphere}} = 0.414.$

2.4. RADIUS RATIO

As pointed out earlier, the ratio of radius of octahedral void to the radius of spheres forming the close-packed arrangement is equal to 0.414 and in case of tetrahedral voids, this ratio is equal to 0.225. In crystals, generally the anions (larger ions) form a close-packed arrangement and the cations fit into the interstitial sites. **The ratio of radius of cation to the radius of anion is known as radius ratio of the ionic solid.** A cation would fit exactly into an octahedral void and would have co-ordination number of six if the radius ratio r^+/r^- were exactly 0.414. Similarly, if the ratio r^+/r^- were 0.225, the cations would fit exactly into tetrahedral voids and would have co-ordination number four. (When the radius ratio is more than the minimum value, the close packed arrangement opens up slightly to accommodate the bigger cations). **In crystals, cations tend to get surrounded by the largest possible number of anions.** The co-ordination number of cation is related to the radius ratio ; greater the radius ratio, greater is the co-ordination number of cation.

In order to understand the effect of radius ratio on the co-ordination number, let us consider a situation in which cations fit exactly in the octahedral voids in the close packing of anions [Fig. 2.14 (a)]. Here the co-ordination number of cations is six. This will be possible when the radius ratio r^+/r^- is 0.414. When the radius ratio is greater than this, the anions move apart to accommodate the larger cation. This situation [Fig. 2.14 (b)] is relatively unstable. If the radius ratio is further increased the anions will move farther and farther apart till finally a stage is reached when more anions can be accommodated. Now the bigger cation moves to bigger void, *i.e.*, cubic void and the co-ordination number increases to eight. This happens when the radius ratio exceeds 0.732.

In case the radius ratio becomes less than 0.414, the six anions will not be able to touch the smaller cation. In their attempt to touch the cation they start overlapping each other [Fig. 2.14 (c)]. This situation is unstable and hence the smaller cation moves to smaller void, *i.e.*, tetrahedral void and the co-ordination number decreases to four.

Thus, for a particular co-ordination number there are higher and lower limiting radius ratios. The lower limiting radius ratio corresponds to packing type a whereas the higher limiting value corresponds to packing type b (Fig. 2.14).

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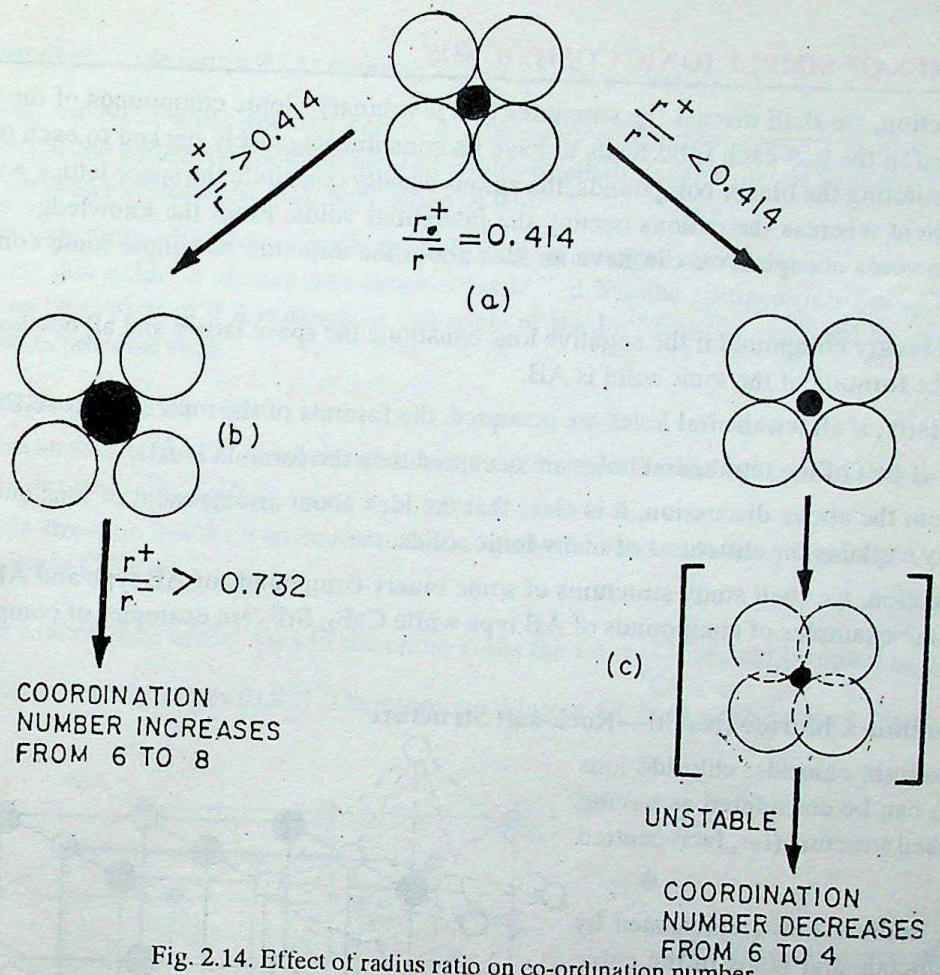

Fig. 2.14. Effect of radius ratio on co-ordination number.

If the radius ratio is in the range 0.225—0.414, the tetrahedral voids are occupied and the co-ordination number is 4. This type of arrangement may give rise to zinc blende structure for the binary compounds of AB type.

If the radius ratio is in the range 0.414—0.732, the octahedral voids are occupied. This type of arrangement gives rise to rock-salt structure in which co-ordination number of cation is 6.

If the radius ratio is in the range 0.732—1, cubic voids are occupied by cations generating a CsCl-type lattice with a co-ordination number of 8.

Radius Ratios in Crystals

Radius ratio r^+/r^-	*Co-ordination Number*	*Structural Arrangement*	*Example*
0.155—0.225	3	Plane triangular	Boron oxide
0.225—0.414	4	Tetrahedral	Zinc sulphide
0.414—0.732	6	Octahedral	Sodium chloride
0.732—1.00	8	Cubic	Caesium chloride

It may be mentioned here that, although large number of ionic substances obey this rule, there are many exceptions to this rule.

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2.5. STRUCTURES OF SIMPLE IONIC COMPOUNDS

In this section, we shall discuss the structures of a few binary* ionic compounds of the type AB and AB_2. As discussed in the text each solid tends to have its constituents closely packed to each other. Among the two ions constituting the binary compounds, the anions usually constitute the space lattice with *hcp* or *ccp* type of arrangement whereas the cations occupy the interstitial voids. From the knowledge of the packed structure and the voids occupied we can have an idea about the structure of simple ionic compounds. For example :

(*i*) For a binary compound if the negative ions constitute the space lattice and all octahedral holes are occupied, then the formula of the ionic solid is AB.

(*ii*) Similarly, if all tetrahedral holes are occupied, the formula of the ionic solid is A_2B.

(*iii*) Now if half of the tetrahedral holes are occupied then the formula is AB.

Thus, from the above discussion, it is clear that the idea about arrangement of ions quite reasonably and satisfactorily explains the structures of many ionic solids.

In this section, we shall study structures of some binary compounds of AB type and AB_2 type. NaCl, CsCl, ZnS, etc. are examples of compounds of AB type while CaF_2, SrF_2 are examples of compounds of AB_2 type.

Structure of Sodium Chloride (NaCl)—Rock-salt Structure

(*i*) In sodium chloride, chloride ions (denoted by ●) can be considered as having cubic close packed structure (*i.e.*, face-centred cubic).

(*ii*) The sodium ions (represented by O) occupy the octahedral holes in the cubic close packed type lattice of chloride ions (Fig. 2.15).

(*iii*) Since there are six octahedral holes around each chloride ion, therefore, each chloride ion is surrounded by six sodium ions. Similarly, each sodium ion is surrounded by six chloride ions (Fig. 2.15). Therefore, in NaCl co-ordination no. of Cl^- ion is 6 and that of Na^+ ions is also 6. This is called 6 : 6 co-ordination.

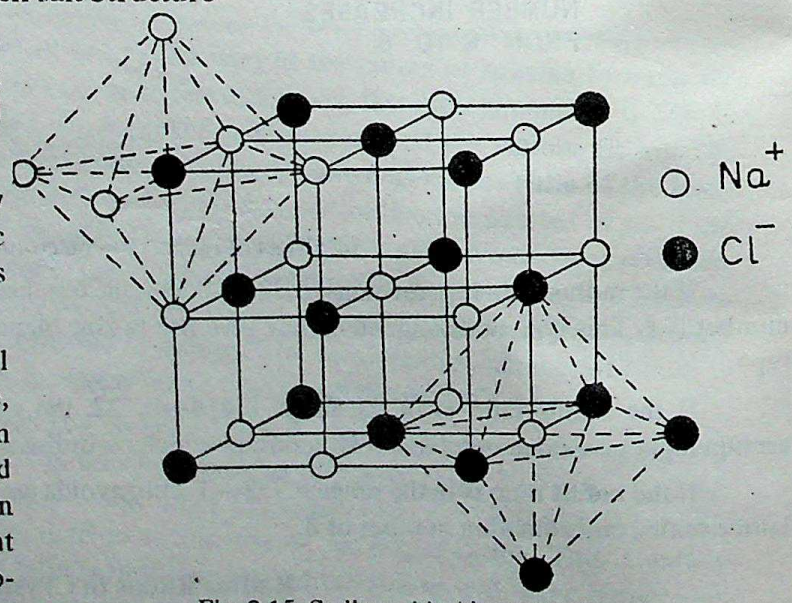

Fig. 2.15. Sodium chloride structure.

(*iv*) It may be pointed out here that for precise fit the ratio of the radii of the two ions $\left(\frac{r_{Na^+}}{r_{Cl^-}}\right)$ should be equal to 0.414. Actually, the ratio $\left(\frac{r_{Na^+}}{r_{Cl^-}} = 0.525\right)$ exceeds this value and as a result the arrangement of Cl^- ions slightly opens up to accommodate sodium ions. Thus, Cl^- ions do not touch each other and form an expanded face centred lattice.

(*v*) The unit cell of sodium chloride has 4 sodium ions and 4 chloride ions as calculated below :

Number of sodium ions = 12 (At edge centres) $\times \frac{1}{4}$ + 1 (At body centre) $\times$ 1 = 4

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* Binary ionic compounds are those which contain two elements.

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Number of chloride ions = 8 (At corners) $\times \frac{1}{8}$ + 6 (At face centres) $\times \frac{1}{2} = 4$

Thus, no. of NaCl units per unit cell is 4. The sodium chloride structure is also called **rock-salt structure**. Most of the halides of alkali metals and oxides of alkaline-earth metals have this type of structure. Some of the common examples are NaI, KCl, RbI and RbF.

FeO also has rock-salt structure in which oxide ions are arranged in *ccp* and Fe^{2+} ions occupy octahedral voids. However, this oxide is always non-stoichiometric d has the composition $Fe_{0.95}O$ (*wustite*). This composition can be explained if it is assumed that some of the Fe^{2+} ions are replaced by two-third as many Fe^{3+} ions, in the octahedral void.

Caesium Chloride (CsCl) Structure

(*i*) In this structure, the Cl^- ions are at the corners of a cube whereas Cs^+ ion is at the centre of the cube or *vice versa* as shown in Fig. 2.16.

(*ii*) This structure has 8 : 8 co-ordination, *i.e.*, each Cs^+ ion is touching eight Cl^- ions and each Cl^- ion is touching eight Cs^+ ions.

(*iii*) For exact fitting of Cs^+ ions in the cubic voids the ratio $\frac{r_{Cs^+}}{r_{Cl^-}}$ should be equal to 0.732, however, actually the ratio is slightly larger (0.93). Therefore, packing of Cl^- ions slightly opens up to accommodate Cs^+ ions.

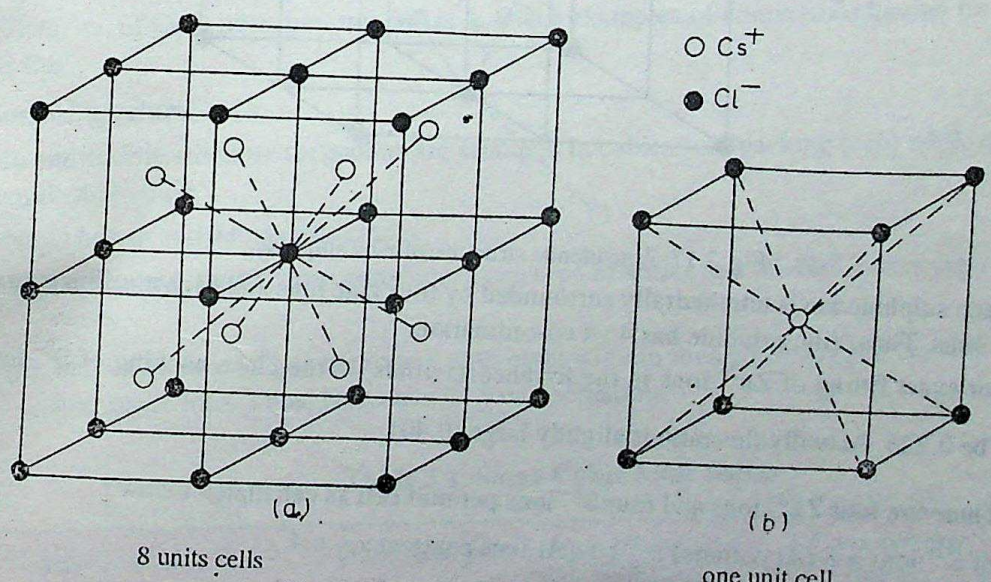

Fig. 2.16. Caesium chloride structure.

(*iv*) The unit cell of caesium chloride has one Cs^+ ion and one Cl^- ion as calculated below :

No. of Cl^- ions = 8 (At corners) $\times \frac{1}{8} = 1$

No. of Cs^+ ion = 1 (At the body centre) $\times$ 1 = 1

Thus, no. of CsCl units per unit cell is 1.

Examples of the compounds having this type of structure are CsBr, CsI, TlCl and TlBr.

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It may be mentioned here that temperature and pressure also affect the structure of an ionic solid. For example, at ordinary temperatures and pressures, chlorides, bromides and iodides of lithium, sodium, potassium and rubidium possess the NaCl structure with 6 : 6 co-ordination. It is observed that on application of high pressure they transform to the CsCl structure with 8 : 8 co-ordination. Thus, high pressure increases the co-ordination number. On the other hand, CsCl on heating transforms to the NaCl structure at 760 K. Thus, at higher temperature co-ordination number decreases.

Zinc Blende Structure (Zinc Sulphide)

(*i*) In zinc blende-structure, sulphide ions (represented by ●) have cubic closed packed (or face-centred cubic) lattice and zinc ions (represented by O) occupy half of the total number of tetrahedral voids as shown in Fig. 2.17.

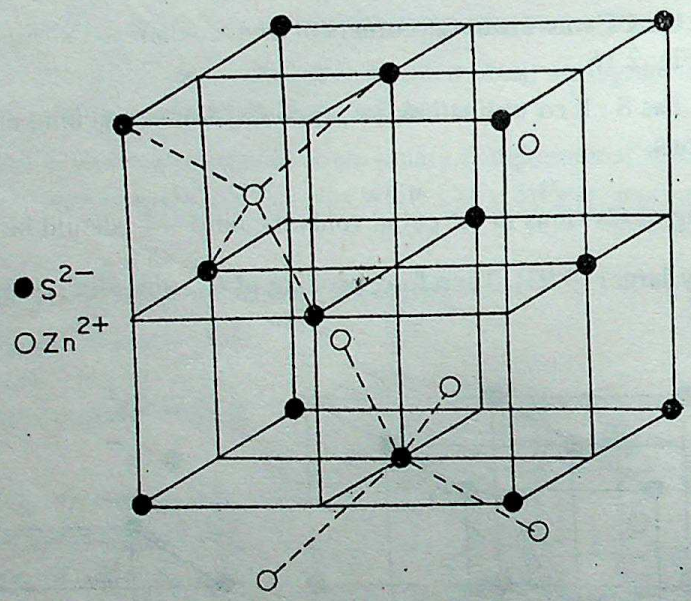

Fig. 2.17. Zinc blende structure of zinc sulphide.

(*ii*) Each sulphide ion is tetrahedrally surrounded by four zinc ions and each zinc ion is surrounded by four sulphide ions. Thus, zinc sulphide has 4 : 4 co-ordination.

(*iii*) For exact fitting of Zn^{2+} ions in the tetrahedral voids, in the close packing of S^{2-} ions, the ratio $\frac{r_{Zn^{2+}}}{r_{S^{2-}}}$ should be 0.225. Actually this ratio is slightly large (0.40).

(*iv*) There are four Zn^{2+} ions and four S^{2-} ions per unit cell as calculated below :

No. of S^{2-} ions = 8 (At corners) $\times \frac{1}{8}$ + 6 (At face centres) $\times \frac{1}{2}$ = 4

No. of Zn^{2+} ions = 4 (Within the body) × 1 = 4

Thus, the number of ZnS units per unit cell is equal to 4.

Some more examples of ionic solids having zinc blende structure are CuCl, CuBr, CuI, AgI.

Fluorite Structure (Calcium fluoride)

(*i*) In CaF_2, Ca^{2+} ions may be considered as having face centred cubic lattice. The fluoride ions occupy all the tetrahedral voids in the lattice of Ca^{2+} ions, as shown in Fig. 2.18.

(*ii*) In this each Ca^{2+} is in contact with eight fluoride ions and each fluoride ion is in contact with four calcium ions. Thus co-ordination no. of Ca^{2+} ions is 8 and that of fluoride ions is 4. Thus, calcium fluoride has 8 : 4 co-ordination.

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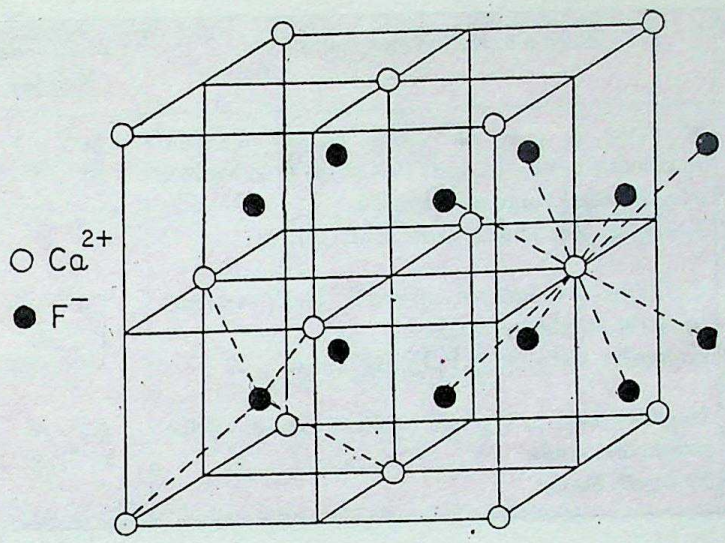

Fig. 2.18. Fluorite structure. Structure of calcium fluoride.

(*iii*) In calcium fluoride each unit cell has four calcium ions and eight fluoride ions explained as under :

No. of calcium ions = 8 (At corners) $\frac{1}{8}$ + 6 (At face centre) × $\frac{1}{2}$ = 4

No. of fluoride ions = 8 (Within the body) × 1 = 8

Thus, no. of CaF_2 units per unit cell is 4. Other examples of compounds having fluorite structure are SrF_2 and CdF_2.

Antifluorite Structure

In antifluorite structure the anions are arranged in cubic close packing (*ccp*) while the cations occupy all the tetrahedral voids.

Na_2O has an antifluorite structure :

(*i*) In this case, the O^{2-} ions constitute a *ccp* type of lattice and the Na^+ ions occupy all the tetrahedral voids.

(*ii*) The oxide ion, O^{2-}, is in contact with eight sodium ions whereas each Na^+ ion is in contact with four oxide ions. Thus, Na_2O has 4 : 8 co-ordination.

Table 2.1. Some Cubic Ionic Solids

Crystal Structure	*Brief description and examples*	*Co-ordination Number*	*No. of formula units per unit cell*
1. **Rock salt (NaCl-type)**	Cl^- ions in *ccp*, Na^+ ions occupy all the octahedral voids (or *vice versa*). *Examples.* Halides of Li, Na, K and Rb, AgCl, AgBr, NH_4Cl, etc.	Na^+ – 6 Cl^- – 6	4
2. **CsCl-type**	Cl^- ions at the corners of a cube and Cs^+ ions in the cubic void (or *vice versa*). *Examples.* CsCl, CsBr, CsI, etc.	Cs^+ – 8 Cl^- – 8	1

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Crystal Structure	*Brief description and examples*	*Co-ordination Number*	*No. of formula units per unit cell*
3. **Zinc-blende (ZnS-type)**	S^{2-} ions in *ccp*, Zn^{2+} ions occupy alternate tetrahedral voids, *i.e.*, only half of the total number of tetrahedral voids are occupied. *Examples.* ZnS, CuCl, CuBr, CuI, AgI, etc.	Zn^{2+} – 4 S^{2-} – 4	4
4. **Fluorite Structure (CaF_2-type)**	Ca^{2+} ions (+ ve ions) in *ccp* and F^- ions (– ve ions) in all the tetrahedral voids. *Examples.* CaF_2, SrF_2, BaF_2, $BaCl_2$, etc.	Ca^{2+} – 8 F^- – 4	4
5. **Antifluorite Structure**	Negative ions in *ccp* and positive ions in all the tetrahedral voids. *Example.* Na_2O.	Na^+ – 4 O^{2-} – 8	4

Normal Spinel Structure

Spinel is a mineral $MgAl_2O_4$. In it oxide ions are arranged in *ccp* with Mg^{2+} ions occupying tetrahedral voids and Al^{3+} ions in a set of octahedral voids. Many *ferrites*, (such as $ZnFe_2O_4$) also possess spinel structure. These are very important magnetic materials and are used in telephones and memory-loops in computers.

Structure of Fe_3O_4 (*Magnetite*)

In Fe_3O_4, Fe^{3+} and Fe^{2+} ions are present in the ratio 2 : 1. It may be considered as having composition FeO Fe_2O_3. In Fe_3O_4 oxide ions are arranged in *ccp*. Fe^{2+} ions occupy octahedral voids while Fe^{3+} ions are equally distributed between octahedral and tetrahedral voids.

$MgFe_2O_4$ also has structure similar to magnetite. In this Mg^{2+} ions are present in place of Fe^{2+} ion in Fe_3O_4.

Magnetite has *inverse spinel structure.*

Example 2.2. *The edge length of a cubic crystal of an element is found (by X-ray diffraction) to be 'a' picometers. Show how can you calculate its density.*

Solution. Edge of unit cell $= a \text{ pm} = a \times 10^{-10} \text{ cm}$

Volume of the unit cell $= a^3 \times 10^{-30} \text{ cm}^3$

Mass of the unit cell = Number of atoms in the unit cell × Mass of each atom

$= z \times m$

Mass of each atom $(m) = \dfrac{\text{Atomic mass}}{\text{Avogadro number}} = \dfrac{M}{N_0}$

Density of the unit cell $= \dfrac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$

Density of the unit cell $= \dfrac{z \times M}{a^3 \times N_0 \times 10^{-30}} \text{ g cm}^{-3}$

If '*a*' is in pm, then density will come out in g/cm^3. The density of the unit cell is the same as the density of the substance.

Example 2.3. *An element having atomic mass 52, occurs in body centred cubic (bcc) structure with a cell edge of 288 pm. The density of the element is 7.2 g cm^{-3}. Evaluate Avogadro's number.*

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Solution. Edge length of unit cell = 288 pm = 288×10^{-10} cm

Volume of the unit cell $= (288 \times 10^{-10}\ \text{cm})^3$

$= 23.9 \times 10^{-24}\ \text{cm}^3$

A body centred unit cell contains two atoms.

Mass of the unit cell = No. of atoms in the unit cell × Mass of one atom

$$= 2 \times \frac{52}{N_0}\ \text{g}$$

Density of the unit cell $= \dfrac{\text{Mass of the unit cell}}{\text{Volume of the unit cell}}$

$$= \frac{2 \times 52\ \text{g}}{N_0 \times 23.9 \times 10^{-24}\ \text{cm}^3}$$

The density of the unit cell is same as the density of the element.

$$\therefore \quad \frac{2 \times 52}{N_0 \times 23.9 \times 10^{-24}}\ \text{g/cm}^3 = 7.2\ \text{g/cm}^3$$

$$N_0 = \frac{2 \times 52}{23.9 \times 10^{-24} \times 7.2} = \mathbf{6.04 \times 10^{23}}.$$

Example 2.4. *A compound formed by elements A and B crystallizes in the cubic structure where A atoms are at the corners of the cube and B atoms are at the centre of the cube. What is the formula of the compound ?*

Solution. An atom at the corner of the cube is shared by 8 cubes and hence contributes only 1/8 to a particular cube. There are eight corners of a cube.

$\therefore$ Number of atoms of A in the unit cell $= 8 \times \frac{1}{8} = 1$.

An atom at the centre of cube belongs only to one unit cell.

$\therefore$ Number of atoms of B in the unit cell $= 1 \times 1 = 1$.

Therefore, formula of the compound is **AB**.

Example 2.5. *An element having atomic mass 60 has face centred cubic unit cells. The edge length of the unit cell is 400 pm. Find out density of the element.*

Solution. Unit cell edge length $= 400\ \text{pm} = 400 \times 10^{-10}$ cm

Volume of unit cell $= (400 \times 10^{-10}\ \text{cm})^3 = 64 \times 10^{-24}\ \text{cm}^3$

Mass of the unit cell = Number of atoms in the unit cell × mass of each atom

Number of atoms in the *fcc* unit cell $= 8 \times \frac{1}{8} + 6 \times \frac{1}{2} = 4$

Mass of one atom $= \dfrac{\text{Atomic mass}}{\text{Avogadro's number}} = \dfrac{60}{6.02 \times 10^{23}}$

$\therefore$ Mass of the unit cell $= 4 \times \dfrac{60}{6.02 \times 10^{23}}$

Density of unit cell $= \dfrac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

$$= \frac{4 \times 60}{6.02 \times 10^{23}} \times \frac{1}{64 \times 10^{-24}} = \mathbf{6.2\ g\ cm^{-3}}.$$

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Example 2.6. *KF has rock-salt structure. Calculate the value of Avogadro's number from the following data :*

Density of KF = 2.48 g cm^{-3}.

Distance between K^+ and F^- in KF = 268 pm.

Solution. Edge length of unit cell in rock salt structure

$$= 2\,(r_c + r_a)$$

Edge length in KF $= 2\,(r_{K^+} + r_{F^-})$

$$= 2\,(268 \text{ pm}) = 536 \text{ pm}$$

Volume of unit cell

$$(536 \times 10^{-10} \text{ cm})^3 = 154 \times 10^{-24} \text{ cm}^3$$

In rock-salt structure one unit cell has 4 formula units of the salt.

$\therefore$ Mass of unit cell $= \dfrac{4 \times \text{Formula mass of KF}}{N_0 \text{ (Avogadro's number)}} = \dfrac{4 \times 58}{N_0}$ g

Density $= \dfrac{\text{Mass of unit cell}}{\text{Volume of unit cell}} = \dfrac{4 \times 58 \text{ g}}{N_0 \times 154 \times 10^{-24} \text{ cm}^3}$

But density of KF is given equal to 2.48 g cm^{-3}

$$\therefore \quad 2.48 = \frac{4 \times 58}{N_0 \times 154 \times 10^{-24}}$$

$$N_0 = \frac{4 \times 58}{154 \times 2.48 \times 10^{-24}} = \mathbf{6.07 \times 10^{23}}.$$

Example 2.7. *An element (density 6.8 g cm^{-3}) occurs in BCC structure with cell edge of 290 pm. Calculate the number of atoms present in 200 g of the element.* (P.S.E.B. 1992)

Solution. In a body centred cubic (BCC) structure there are two atoms per unit cell.

Let M be the gram molecular mass of the element

Mass per unit cell = Number of atoms in the unit cell × Mass per atom

$$= 2 \times \frac{M}{6.02 \times 10^{23}}$$

Volume of the unit cell $= (290 \times 10^{-10} \text{ cm})^3 = 24.4 \times 10^{-24} \text{ cm}^3$

Density $= \dfrac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

Density is given as 6.8 g cm^{-3}.

$$\therefore \quad 6.8 = \frac{2 \times M}{6.02 \times 10^{23} \times 24.4 \times 10^{-24}}$$

$$M = \frac{6.8 \times 6.02 \times 10^{23} \times 24.4 \times 10^{-24}}{2} = 50 \text{ g}$$

Thus, gram molecular mass of the element is 50 g.

$\therefore$ 50 g of the element contain 6.023×10^{23} atoms

200 g of the element would contain $= \dfrac{6.023 \times 10^{23} \times 200}{50} = \mathbf{24.09 \times 10^{23}}$ **atoms**

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Example 2.8. *An element crystallizes in a structure having a FCC unit cell of an edge 200 pm. Calculate its density, if 200 g of this element contains 24×10^{23} atoms.* (A.I. CBSE 1991)

Solution. Edge length $= 200$ pm

Volume of the unit cell $= (200 \times 10^{-10}\ \text{cm})^3 = 8 \times 10^{-24}\ \text{cm}^3$

In a FCC unit cell there are four atoms per unit cell.

$\therefore$ Mass of unit cell $= \dfrac{200 \times 4}{24 \times 10^{23}} = 33.3 \times 10^{-23}$ g

Density $= \dfrac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

$= \dfrac{33.3 \times 10^{-23}\ \text{g}}{8 \times 10^{-24}\ \text{cm}^3} = \mathbf{41.6\ g\ cm^{-3}}$.

Example 2.9. *Iron has body centred cubic lattice structure. The edge length of the unit cell is found to be 286 pm. What is the radius of an iron atom ?*

Solution. In a body centred cubic unit cell the atoms at the corners do not touch each other but are touching the atom at the centre. In such a unit cell, the body diagonal is four times the atomic radius.

Body diagonal $= \sqrt{3}$. Edge length

$= \sqrt{3} \times 286 = 495$ pm

Atomic radius $= \dfrac{\text{Body diagonal}}{4} = \dfrac{495}{4} = \mathbf{124\ pm.}$

Example 2.10. *Copper crystal has a face centred cubic lattice structure. Atomic radius of copper atom is 128 pm. What is the density of copper metal ? Atomic mass of copper is 63.5.*

Solution. In face centred cubic arrangement face diagonal is four times the radius of atom.

Face diagonal $= 4 \times 128 = 512$ pm

Face diagonal $= \sqrt{2} \times$ Edge length

Edge length $= \dfrac{512}{\sqrt{2}} = 362$ pm

$= 362 \times 10^{-10}$ cm

Volume of the unit cell $= (362 \times 10^{-10})^3\ \text{cm}^3$

$= 47.4 \times 10^{-24}\ \text{cm}^3$

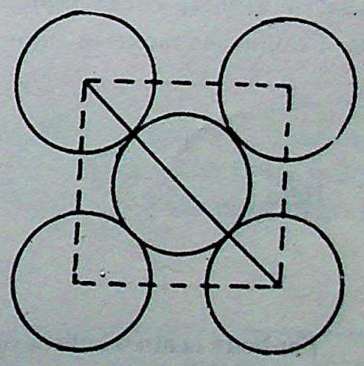

Fig. 2.19

In a face centred cubic unit cell, there are four atoms per unit cell.

Mass of unit cell $= \dfrac{4 \times 63.5}{6.02 \times 10^{23}}\ \text{g} = 4.22 \times 10^{-22}$ g

Density $= \dfrac{\text{Mass of unit cell}}{\text{Volume of unit cell}}$

$= \dfrac{4.22 \times 10^{-22}\ \text{g}}{47.4 \times 10^{-24}\ \text{cm}^3} = \mathbf{8.9\ g\ cm^{-3}}$.

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REVIEW PROBLEMS

2.1. MgO has NaCl structure and its unit cell edge is 421 pm. What is its density ?

2.2. CuCl has zinc blende structure. Its density is 3.4 g cm^{-3}. Calculate the length of its unit cell edge.

2.3. KF has rock-salt structure. Calculate edge length of its unit cell, if its density is 2.48 g cm^{-3}.

2.4. Strontium oxide (SrO) crystal has cubic structure and has density 5 g cm^{-3}. If edge of the unit cell has length 520 pm, calculate the number of SrO formula units in each unit cell. At. mass of Sr = 88.

2.5. Edge length of NaCl crystal is 562 pm and density of NaCl is 2.165 g cm^{-3}. Calculate the value of Avogardro number.

2.6. Copper crystal has a face-centred cubic lattice structure. Its density is 8.93 g cm^{-3}. What is the length of the unit cell ? ($N = 6.023 \times 10^{23}$, Atomic mass of Cu = 63.5) *[CBSE (I) 1992]*

2.7. The density of a face centred cubic element (atomic mass = 60.2) is 6.25 g cm^{-3}. Calculate the length of edge of the unit cell. *[Har. (Sc) 1992]*

2.8. Lead (II) sulphide crystal has NaCl structure. What is its density ? The edge length of the unit cell of PbS crystal is 500 pm. ($N = 6.023 \times 10^{23}$ mol^{-1}, Atomic masses : Pb = 207.2, S = 32). *(A.I. CBSE 1993)*

2.6. IONIC RADII

With the help of X-ray or electron diffraction, it is possible to determine the dimensions of unit cells. From the dimensions of the unit cell it is possible to calculate ionic radii (assuming ions to be spheres and touching each other). For example, edge of a unit cell in sodium chloride structure (Fig. 2.15) is related to the radius of cation and radius of anion as :

$$2r_c + 2r_a = a$$

$$r_c + r_a = a/2$$

Here, r_c = radius of cation

r_a = radius of anion

a = edge length of the unit cell.

For body centred lattices of the CsCl type, the interionic distance is given as

$$r_c + r_a = \frac{\sqrt{3}}{2} a$$

Thus, knowing the type of the unit cell, edge length of the unit cell and the radius of one of the ions (either cation or anion) the radius of the other ion can be calculated. There are several methods of calculating the radii of the ions theoretically from the internuclear distances. One such method is Pauling's method. Details of this method are beyond the scope of this book.

Ionic radii of some ions as obtained by Pauling are given in Table 2.2.

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Table 2.2. Ionic Radii of Some Common Ions

Cations	*Ionic Radii (pm)*	*Anion*	*Ionic Radii (pm)*
Li^+	60	F^-	136
Na^+	95	Cl^-	181
K^+	133	Br^-	195
Rb^+	148	I^-	216
Cs^+	169	O^{2-}	140
Mg^{2+}	65	S^{2-}	184
Ca^{2+}	99	Se^{2-}	198
Al^{3+}	50	Te^{2-}	221

The observed values of interionic distances are quite in agreement with the calculated values from ionic radii as shown in Table 2.3.

Table 2.3. Comparison Between Observed and Calculated Values of Interionic Distances

Substance	*Interionic Distance (in pm)*	
	Observed	*Calculated (By adding ionic radii)*
NaCl	281	276
KCl	314	314
RbCl	329	329
CsCl	347	350

Trends in ionic radii. The ionic radii increase in a group with increase in atomic number. For example, for alkali metals, the ionic radii are in the order $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ and for halogens the order is $I^- > Br^- > Cl^- > F^-$. Among isoelectronic ions the ionic radius decreases with increase in nuclear charge. For example, ionic radii decrease in the order $O^{2-} > F^- > Na^+ > Mg^{2+} > Al^{3+}$.

2.7. SILICATES

Metal silicates have wide range of structures from simple monomers to complex polymers, but the basic unit of all the silicates is the SiO_4^{4-} tetrahedron. These tetrahedra occur singly, or by sharing oxygen atoms, in small groups, in small cyclic groups, in infinite chains or infinite sheets.

1. **Simple orthosilicates.** In these silicates, SiO_4 tetrahedra do not share oxygen atoms with one another and exist as discrete SiO_4^{4-}, orthosilicate anions Fig. 2.20 (*a*). For example, Mg_2SiO_4, Fe_2SiO_4 and Zn_2SiO_4. In these compounds SiO_4^{4-} ion is linked to M^{2+} ions through co-ordinate bond.

2. **Pyrosilicates or islands.** When two SiO_4 tetrahedra share a common oxygen, island structures having formula $(Si_2O_7)^{-6}$ are obtained Fig. 2.20 (*b*). Pyrosilicates are examples of this type of silicates.

3. **Ring or cyclic silicates anions.** Ring anions are obtained when two oxygen atoms of each tetrahedron are shared with others. $(Si_3O_9)^{6-}$ and $(Si_6O_{18})^{12-}$ Fig. 2.20 (*c*) and (*d*) are typical ring anions. General formula of any such anion must be $(Si_nO_{3n})^{2n-}$.

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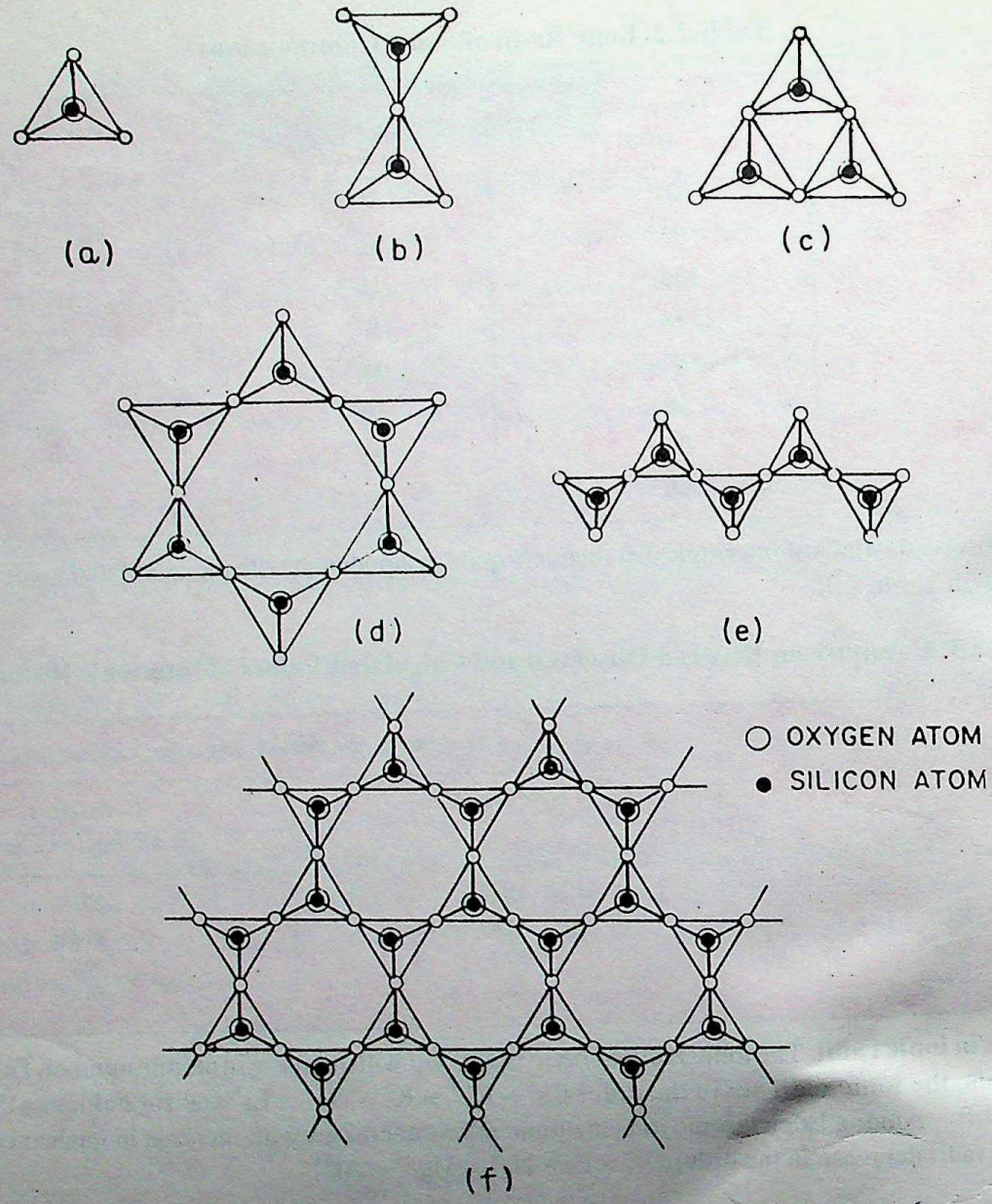

Fig. 2.20. *Anions in silicate structures* (*a*) SiO_4^{4-} (*b*) $(Si_2O_7)^{6-}$ (*c*) $(Si_3O_9)^{6-}$ (*d*) $(Si_6O_{18})^{12-}$ (*e*) $(SiO_3^{2-})_n$ *chain* (*f*) $(Si_2O_5^{2-})_n$ *layer.*

4. **Infinite chain silicates.** These are of two types, the pyroxenes which contain single-strand chains of composition $(SiO_3^{2-})_n$ Fig. 2.20 (*e*) and amphiboles which contain double-strand, cross-linked chains of composition $(Si_4O_{11}^{6-})_n$. General formula of the anion in a pyroxene is the same as in a silicate with cyclic anion. Diopside ($MgCaSi_2O_6$) is an example of pyroxene. Various asbestos minerals are also examples of chain silicates (amphiboles).

5. **Infinite sheet silicates.** Two dimensional sheet structures are obtained when **three oxygen** atoms of each SiO_4 tetrahedron are shared. The general formula of the anion in sheet structure is $(Si_2O_5^{2-})_n$. Clay is an example of sheet structure.

6. **Framework silicate.** Three dimensional network is obtained when all the four oxygen atoms of each of SiO_4 tetrahedron are shared. Quartz and zeolites are examples of framework silicates. The general formula of framework silicates is SiO_2.

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2.8. IMPERFECTIONS IN SOLIDS

At absolute zero, crystals tend to have a perfectly ordered arrangement. This arrangement corresponds to state of lowest energy. As the temperature increases, the crystals start deviating from the perfectly ordered arrangement. *Any deviation from the perfectly ordered arrangement constitutes a* **defect** or **imperfection.** These defects are sometimes called **thermodynamic defects** because the number of these defects depends on the temperature. Crystals may also possess additional defects due to the presence of impurities. Many properties of crystalline solids such as electrical conductivity and mechanical strength can be explained in terms of imperfections. Imperfections not only modify the properties of solids but also give rise to new properties.

1. Electronic Imperfections

In a perfectly covalent or ionic crystal (such as that of Si or NaCl) at 0 K, electrons are present in fully occupied lowest energy states. However, at higher temperatures, some of the electrons may occupy higher energy states depending upon the temperature. For example, in crystals of pure silicon or germanium some electrons are released thermally from the covalent bonds at temperatures above 0 K. These electrons are free to move in the crystal and are responsible for electrical conductivity. This type of conduction is known as **intrinsic conduction.** *The electron deficient bond formed by the release of an electron* is called a **hole.** Holes also give rise to electrical conductivity. In the presence of electric field the positive holes move in a direction opposite to that of the electrons. Electrons and holes in solids constitute **electronic imperfections.** Concentrations of electrons (**e**) and holes (**h**) are designated by symbols **n** and **p** respectively. In pure crystals of silicon and germanium the concentrations of electrons and holes will be equal. Electrons or holes can be preferentially created in such covalent crystals by addition of certain impurities. This has been discussed in the following article.

2. Atomic Imperfections

The defects which arise due to the irregularity in the arrangement of atoms or ions are called **atomic imperfections.** The atomic defects caused by missing or misplaced ions are called **point defects.** If the deviations from periodicity extend over microscopic regions of the crystal they are called **lattice imperfections.** Lattice imperfections may extend along lines (*line defects*) or planes (*plane defects*). Line defects are also called *dislocations.* Let us discuss various types of point defects.

Stoichiometric point defects. The compounds in which the numbers of positive and negative ions are exactly in the ratios indicated by their chemical formulae are called stoichiometric compounds. The defects that do not disturb the stoichiometry (the ratio of numbers of positive and negative ions) are called *stoichiometric defects.* These are of following types :

(*a*) *Schottky Defects.* This type of defect is created when one positive ion and one negative ion are missing from their respective positions leaving behind a pair of *holes* (Fig. 2.21). Schottky defects are more common in ionic compounds with high co-ordination number, and where the sizes of positive and negative ions are almost equal. For example, NaCl, KCl, CsCl and KBr.

NaCl has one defect in 10^{15} lattice sites at room temperature. The number of defects increases with increase in temperature. The number of defects increases to one in 10^6 sites at 775 K and one in 10^4 sites at 1075 K. The presence of large number of Schottky defects in crystal results in significant decrease in its density.

(*b*) *Interstitial Defects.* This type of defect is caused due to the presence of ions in the normally vacant interstitial sites in the crystal. The ions occupying the interstitial sites are called **interstitials.** The formation of interstitial defects is determined by the size of the interstitial ion.

(*c*) *Frenkel Defect.* This type of defect is created when an ion leaves its correct lattice site and occupies an interstitial site (Fig. 2.21). Frenkel defects are common in ionic compounds which have low co-ordination number and in which there is large difference in size between positive and negative ions. For example, ZnS, AgCl, AgBr and AgI.

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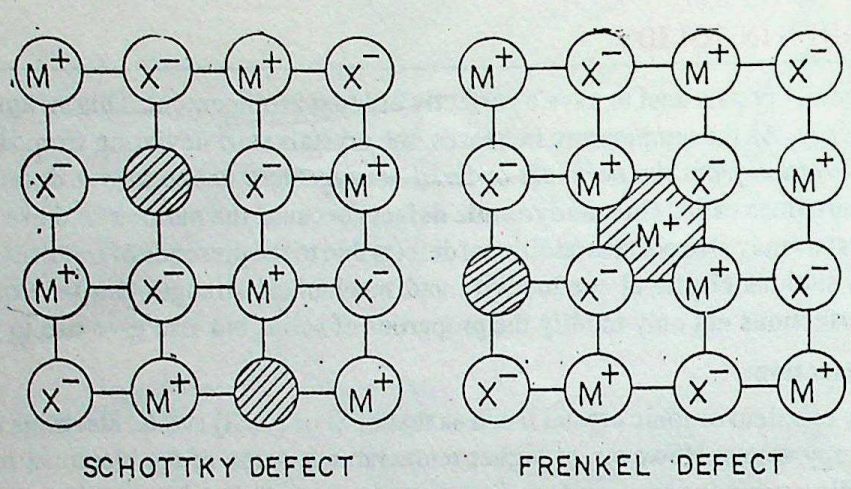


Fig. 2.21. Stoichiometric defects.

Consequences of Stoichiometric defects

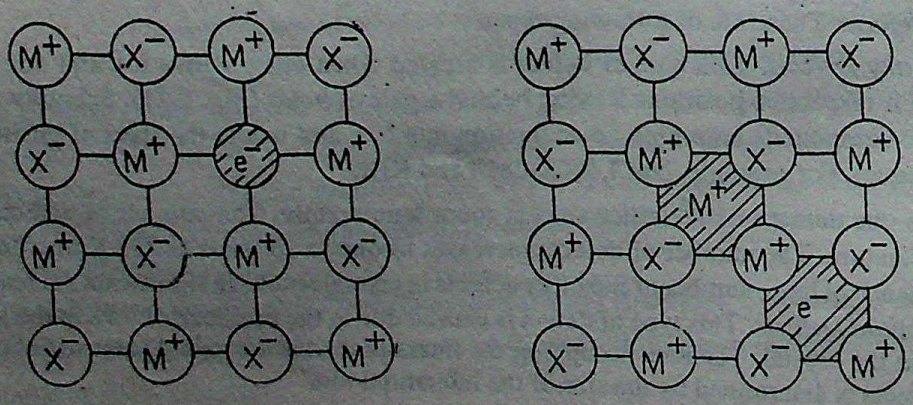
(*i*) The presence of these defects in the crystals make them good electrical conductors.

(*ii*) The presence of holes in Schottky type defects lowers their density.

(*iii*) The presence of ions in interstitial sites in the Frenkel defects increases the dielectric constant of the crystals.

Non-stoichiometric defects. There are many compounds in which the ratio of positive and negative ions present in the compound differs from that required by ideal chemical formula of the compound. Such compounds are called *Non-stoichiometric* or *Berthollide compounds*. In these compounds composition may vary over a wide range. For example, in vanadium oxide (VO_x), x can be anywhere between 0.6 and 1.3. In these compounds balance of positive and negative charges is maintained by having either extra electrons or extra positive charges. This results in defects in the crystal structure. The defects which disturb the stoichiometry of the compound are called **non-stoichiometric defects.** These defects are either due to the presence of excess metal ions or excess non-metal ions.

(*a*) *Metal Excess Defects due to Anion Vacancies.* A compound may have excess metal ion if a negative ion is absent from its lattice site, leaving a '*hole*', which is occupied by electron [Fig. 2.22 (*a*)] to maintain electrical neutrality.



(*a*) Metal excess defect due to anion vacancies.

(*b*) Metal excess defect due to interstitial cation.

Fig. 2.22

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This type of defects are found in crystals which are likely to possess Schottky defects. Anion vacancies in alkali halides are produced by heating the alkali halide crystals in an atmosphere of alkali metal vapours. Under these conditions alkali metal atoms deposit on the surface of the alkali halide crystal, halide ions move to the surface and combine with metal ions. The electrons released during conversion of metal atoms into ions diffuse into the crystal and occupy the sites vacated by anions.

The 'holes' occupied by electrons are called **F-centres** (or colour centres) and are responsible for the colour of the compound and many other interesting properties. For example, the excess sodium in NaCl makes the crystal appear yellow, excess potassium in KCl makes it violet and excess lithium in LiCl makes it pink. Greater the number of F-centres, greater is the intensity of colour. Solids containing F-centres are paramagnetic because the electrons occupying the 'holes' are unpaired.

(*b*) *Metal Excess Defects due to Interstitial Cations*. Another way in which metal excess defects may occur is, if an extra positive ion is present in an interstitial site. Electrical neutrality is maintained by the presence of an electron in the interstitial site [Fig. 2.22 (*b*)]. This type of defects are exhibited by the crystals which are likely to exhibit 'Frenkel' defects. For example, when ZnO is heated, it loses oxygen reversibly. The excess metal is accommodated in interstitial sites, with electrons trapped in the neighbourhood. The yellow colour and the electrical conductivity of the non-stoichiometric ZnO is due to these trapped electrons.

(*c*) *Metal deficiency due to Cation Vacancies*. The non-stoichiometric compounds may have metal deficiency due to the absence of a metal ion from its lattice site. The charge is balanced by an adjacent ion having higher positive charge (Fig. 2.23). This type of defects are generally shown by compounds of transition metals.

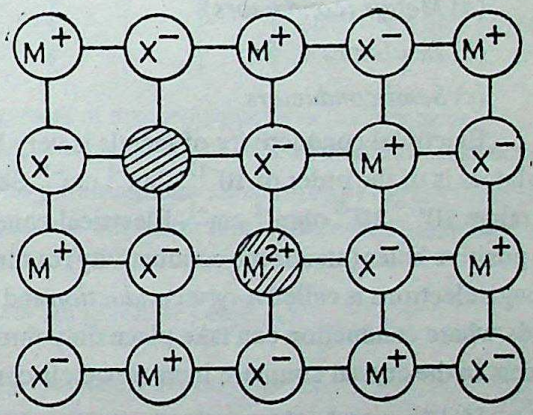

Fig. 2.23. Metal deficiency due to cation vacancy.

It may be mentioned here that metal excess compounds and metal deficient compounds both act as semi-conductors. Metal excess compounds conduct electricity through normal electron conduction mechanism and are therefore **n-type semiconductors**. Metal deficient compounds conduct electricity through positive hole conduction mechanism and are therefore **p-type semi-conductors**.

Point Defects due to the Presence of Foreign Atoms

So far we have discussed point defects where there are no foreign atoms. Foreign atoms can occupy interstitial or substitutional sites in a crystal. Solid solutions of group 13 or group 15 impurities with group 14 elements such as silicon or germanium are of great interest in electronic industry as they are used to make transistors. The group 13 elements such as Al and Ga and the group 15 elements such as P and As form substitutional solid solutions with Si and Ge. The group 15 elements have five valence electrons. After forming the four covalent bonds with the group 14 elements one excess electron is left on them. The excess electrons give rise to electronic conduction (*n-type conduction*). The group 13 elements have only three valence electrons. They combine with group 14 elements

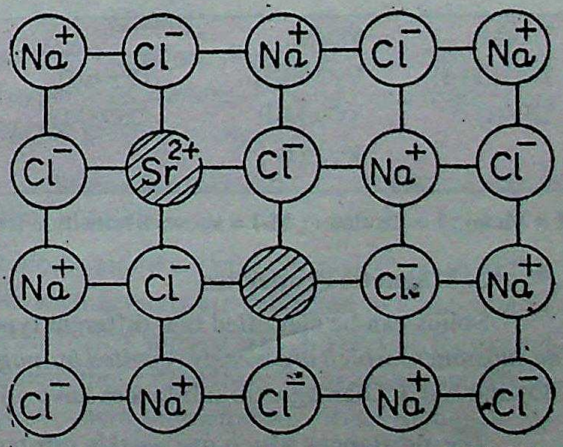

Fig. 2.24. Introduction of cation vacancy in NaCl by substitution of Na^+ with Sr^{2+} ion.

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resulting in the formation of an *electron deficient bond* or a *hole*. These holes give rise to positive hole conduction (*p-type conduction*). Silicon and germanium doped with group 13 or group 15 elements impurities act as *semi-conductors* and have fairly high electrical conductivity. This type of conduction is known as *extrinsic conduction.*

Defects in the ionic solids may be introduced by adding impurity ions. If the impurity ions have different valence state than that of the host ions, vacancies are created. For example, addition of $SrCl_2$ to NaCl yields solids solutions where the divalent cation occupies Na^+ sites and produces cation vacancies equal to the number of the divalent ions occupying substitutional sites (Fig. 2.24).

Similarly, AgCl crystals can be doped with $CdCl_2$ to produce impurity defects in a likewise manner.

2.9. PROPERTIES OF SOLIDS

1. Electrical Properties

On the basis of electrical conductivity the solids can be broadly classified into three types :

(*a*) *Metals (conductors)*

(*b*) *Insulators*

(*c*) *Semi-conductors.*

Electrical conductivity of metals is very high and is of the order of $10^6 - 10^8$ ohm^{-1} cm^{-1} while that of insulators is of the order of 10^{-12} ohm^{-1} cm^{-1}. Semi- conductors have intermediate conductivity which lies in the range $10^2 - 10^{-9}$ ohm^{-1} cm^{-1}. Electrical conductivity of solids may arise through the motion of electrons and positive holes (electronic conductivity) or through the motion of ions (ionic conductivity). The conduction through electrons is called *n-type conduction* and through positive holes is called *p-type conduction.* Pure ionic solids where conduction can take place only through motion of ions are insulators. However, the presence of defects in the crystal structure increases their conductivity.

Unlike metals, the conductivity of semi-conductors and insulators is mainly due to the presence of interstitial electrons and positive holes in the solids due to imperfections. ***The conductivity of semiconductors and insulators increases with increase in temperature while that of metals decreases.***

The electrical behaviour of some oxides of transition metals (belonging to fourth period) is given in Table 2.4. It may be noted that these oxides show wide variation in their electrical behaviour.

Table 2.4. Electrical Properties of Some Transition Oxides

TiO(M)	VO(M)		MnO(I)	FeO(I)	CoO(I) NiO(I) CuO(I)
Ti_2O_3(M-I)	V_2O_3M(I)	Cr_2O_3(I)	Mn_2O_3(I)	Fe_2O_3(I)	
TiO_2(I)	VO_2(M-I)	CrO_2(M)	MnO_2(I)		
	V_2O_5(I)				

M = Metal ; I = Insulator ; M-I = shows a transition from metal to insulator behaviour at a certain temperature.

2. Magnetic Properties

Solids can be classified into different types depending upon their behaviour towards magnetic fields. *The substances which are weakly repelled by magnetic field* are called **diamagnetic substances.** For example, TiO_2 and NaCl. Diamagnetic substances have all their electrons paired.

The substances which are weakly attracted by magnetic field are called **paramagnetic substances.** These substances have permanent magnetic dipoles due to the presence of some species (atoms, ions or

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molecules) with unpaired electrons. The paramagnetic substances lose their magnetism in the absence of magnetic field. For example, TiO, VO_2 and CuO.

The substances which are strongly attracted by magnetic field are called **ferromagnetic substances.** These substances show permanent magnetism even in the absence of magnetic field. Some examples of ferromagnetic solids are : iron, cobalt, nickel and CrO_2.

Ferromagnetism arises due to spontaneous alignment of magnetic moments of ions or atoms in the same direction [Fig. 2.25 (*a*)]. Alignment of magnetic moments in opposite direction in a compensatory manner and resulting in a zero magnetic moment (due to equal number of parallel and antiparallel magnetic dipoles) gives rise to *antiferromagnetism* [Fig. 2.25 (*b*)]. For example, MnO, Mn_2O_3 and MnO_2 are antiferromagnetic. Alignment of magnetic moments in opposite directions resulting in a net magnetic moment (due to unequal number of parallel and antiparallel magnetic dipoles) gives rise to *ferrimagnetism* [Fig. 2.25 (*c*)]. For example, Fe_3O_4 is ferrimagnetic.

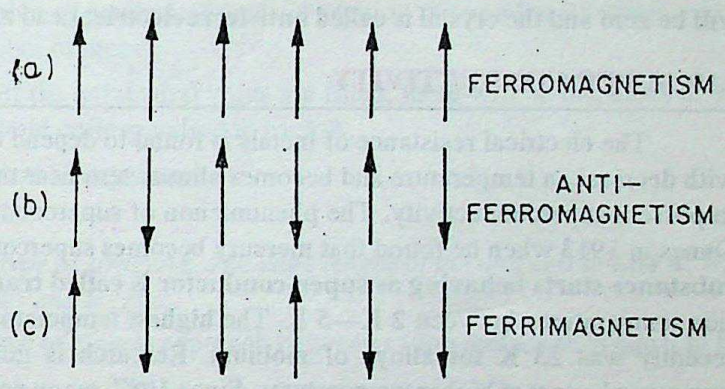

Fig. 2.25. Alignment of magnetic dipoles in (*a*) ferromagnetic, (*b*) antiferromagnetic and (*c*) ferrimagnetic substances.

Ferromagnetic and ferrimagnetic substances change into paramagnetic substances at higher temperatures due to randomisation of spins. Fe_3O_4, which is ferrimagnetic at room temperature, becomes paramagnetic at 850 K.

Magnetic behaviours of some oxides of transition metals are given in Table 2.5.

Table 2.5. Magnetic Properties of Some Transition Metal Oxides

TiO(p)	VO(p)		MnO(af)	FeO(af)	CoO(af) NiO(af) CuO(p)
Ti_2O_3(p)	V_2O_3(af)	Cr_2O_3(af)	Mn_2O_3(af)	Fe_2O_3(af)	
TiO_2(d)	VO_2(p)	CrO_2(f)	MnO_2(af)	Fe_3O_4(fe)	
	V_2O_5(d)				

p = paramagnetic ; af = anti-ferromagnetic ; fe = ferrimagnetic ; f = ferromagnetic ; d = diamagnetic.

3. Dielectric Properties

A **dielectric** *is a substance in which an electric field gives rise to no net flow of electric charge.* This is due to the reason that electrons in a dielectric are tightly held by individual atoms. However, under the effect of applied field displacement of charges takes place, resulting in the creation of dipoles.

The alignment of these dipoles in different ways, *i.e.*, compensatory way (zero dipole) or non-compensatory way (net dipole) impart certain characteristic properties to solids.

The dipoles may align in such a way so that there is net dipole moment in the crystals. Crystals of this type exhibit **piezoelectricity** or **piezoelectric effect**, *i.e.*, when such crystals are subjected to a pressure or mechanical stress, electricity is produced. Conversely, if an electric field is applied to such a crystal, the crystal gets deformed due to generation of mechanical strain. This is sometimes called **inverse piezoelectric effect.** The piezoelectric crystals are used as pickups in record players, where they produce electrical signals by application of pressure.

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Certain crystals, when heated, acquire electric charges on opposite faces. This property of crystals is known as **pyroelectricity.**

There are certain solids in which dipoles are spontaneously aligned in a particular direction, even in the absence of electric field. Such substances are called **ferroelectric substances** and the phenomenon is called **ferroelectricity.** The direction of polarisation in these substances can be changed by applying electric field. Barium titanate ($BaTiO_3$), sodium potassium tartrate (*Rochelle salt*) and potassium hydrogen phosphate (KH_2PO_4) are ferroelectric solids. If the alternate dipoles are in opposite direction, then the net dipole moment will be zero and the crystal is called **anti-ferroelectric.** Lead zirconate ($PbZrO_3$) is an anti-ferroelectric solid.

2.10. SUPER CONDUCTIVITY

The electrical resistance of metals is found to depend on temperature. Electrical resistance decreases with decrease in temperature and becomes almost zero near the absolute zero. Materials in this state are said to possess superconductivity. The phenomenon of superconductivity was first discovered by Kammerlingh Onnes in 1913 when he found that mercury becomes superconducting at 4 K. **The temperature at which a substance starts behaving as super-conductor is called transition temperature.** Most metals have transition temperatures between 2 K—5 K. The highest temperature at which super-conductivity was known till recently was 23 K for alloys of niobium. Research is going on to find materials which behave as a super-conductors at higher temperatures. Since 1987, many complex metal oxides have been found to possess super-conductivity at somewhat higher temperatures. Some of them are listed below :

$YBa_2Cu_3O_7$	90 K
$Bi_2Ca_2Sr_2Cu_3O_{10}$	105 K
$Ti_2Ca_2Ba_2Cu_3O_{10}$	125 K

Super-conducting materials have great technological potential. These can be used in *electronics, in building magnets, in power transmission* and *in levitation transportation* (trains which move in air without rails).

2.11. AMORPHOUS SOLIDS

An **amorphous solid** *is a substance whose constituent particles do not possess a regular orderly arrangement.* Some examples of amorphous solids are glass, plastics, rubber, etc. Quartz is a crystalline form of silica (SiO_2). In it SiO_4 tetrahedra are connected to one another in such a way so that oxygen atom of each SiO_4 tetrahedron is shared with another silicon atom. If quartz or SiO_2 is melted and the melt is cooled, glass is formed which is amorphous. In glass SiO_4 tetrahedra are randomly joined. In a similar way, any crystalline solid can be changed into amorphous solid by melting it and then cooling the molten mass rapidly.

Though amorphous solids do not possess long range regularity, they may possess small regions of orderly arrangement. These *crystalline parts of an otherwise amorphous solid are known as* **crystallites.**

An amorphous solid does not possess a sharp melting point and undergoes liquefaction over a broad range of temperature. That is why glasses and plastics soften over a temperature range and can be moulded or blown into various shapes. Amorphous solids do not possess characteristic heats of fusion.

Uses of Amorphous Solids

Amorphous solids such as glass and plastics are very important materials and are widely used in construction, houseware, laboratory ware, etc. Amorphous silica is likely to be the best material for converting sunlight into electricity (*photovoltaic*).

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SOME MISCELLANEOUS QUESTIONS

Example 2.11. *A solid between A and B has the following arrangement of atoms :*

(i) Atoms A are arranged in c.c.p. array.

(ii) Atoms B occupy all the octahedral voids and half the tetrahedral voids.

What is the formula of the compound ?

Solution. In a close packing the number of octahedral voids is equal to the number of atoms and the number of tetrahedral voids is twice the number of atoms.

Since all the octahedral voids and half the tetrahedral voids are filled, there will be one atom of B in tetrahedral void and one atom in octahedral void corresponding to each A.

Thus, there will two atoms of B corresponding to each A.

Hence, **formula of the solid is AB_2.**

Example 2.12. *A solid AB has CsCl-type of structure. The edge length of the unit cell is 4.04 Å. What is the distance of closest approach between A^+ and B^- ?*

Solution. In CsCl structure the distance of closest approach between cation and anion is equal to half the body diagonal of the cube.

Body diagonal $= \sqrt{3} \times$ Edge length $= \sqrt{3} \times 4.04$ Å $= 7.0$ Å

The distance of closest approach $= \frac{1}{2}$ of the body diagonal $= \frac{1}{2} \times 7.0$ Å $=$ **3.5 Å.**

Example 2.13. *In corrundum, oxide ions are arranged in h.c.p. array and the aluminium ions occupy two-thirds of octahedral voids. What is the formula of corrundum ?*

Solution. In a close packing (h.c.p.) or (c.c.p.) there is one octahedral void corresponding to each atom constituting the close packing.

In corrundum only two-thirds of octahedral voids are occupied. It means corresponding to each oxide ion there are 2/3 aluminium ions. The whole number ratio of oxide and aluminium ion in corrundum is, therefore, 3 : 2.

Hence, **formula of corrundum is Al_2O_3.**

Example 2.14. *Show by simple calculation that the percentage of space occupied by spheres in a simple cubic unit cell is 52.4%.*

Solution. In a simple cubic unit cell there is only one atom per unit cell.

Let a be the edge length of the unit cell and r be the radius of sphere.

Volume of the sphere $= \frac{4}{3}\pi r^3$

As the spheres at the corners are touching each other, the edge length a is equal to $2r$.

Volume of the cube $= a^3 = (2r)^3 = 8r^3$

% of the space occupied by spheres

$$\frac{\text{Volume of sphere}}{\text{Volume of cube}} \times 100$$

$$= \frac{\frac{4}{3}\pi r^3}{8r^3} \times 100 = \frac{4}{3} \times \frac{22}{7} \times \frac{1}{8} \times 100 = \mathbf{52.4\%}.$$

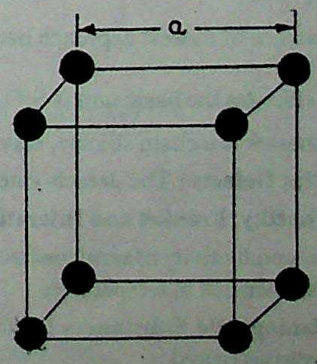

Fig. 2.26

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IMPORTANT TERMS, CONCEPTS AND FORMULAE

- **Solid State :** The state of the substance in which it has definite volume and definite shape.
- **Crystalline Solids :** The substances in which constituent particles have orderly arrangement.
- **Amorphous Solids :** The substances in which constituent particles donot have orderly arrangement.
- **Space Lattice :** A three dimensional orderly arrangement of identical points. This depicts the relative arrangement of constituent particles in the crystal.
- **Unit Cell :** A three dimensional group of lattice points that generates the whole lattice by translation or stacking.
- **Types of Cubic Unit Cells :** Simple, body centred (BCC) and face centred (FCC).
- **Face diagonal** $= \sqrt{2} \times$ Edge length (For Cube).
- **Body diagonal** $= \sqrt{3} \times$ Edge length (For Cube).
- **For FCC arrangement** of atoms, radius of atom, r can be calculated by the formula

$$r = \frac{1}{4} \times \text{Face diagonal} = \frac{1}{4} . \sqrt{2} \times \text{Edge length.}$$

- **For BCC arrangement** of atoms, radius of atom, r can be calculated as :

$$r = \frac{1}{4} \text{Body diagonal} = \frac{1}{4}\sqrt{3} \times \text{Edge length.}$$

- **NaCl Structure :** Cl^- ions have *ccp* arrangement and Na^+ ions occupy all the octahedral voids. C. No. of Na^+ and Cl^- is 6 : 6.
- **Zinc Blende Structure :** S^{2-} ions have *ccp* arrangement and Zn^{2+} ions occupy half the alterate tetrahedral voids. C. No. of Zn^{2+} and S^{2-} is 4 : 4.
- **CsCl-Structure :** Cl^- ions are in cubic arrangement and Cs^+ ions occupy cubic voids. C. No. is 8 : 8.
- **Fluorite Structure :** Ca^{2+} ions (cations) in *ccp* and F^- ions (anions) occupy all the tetrahedral voids. C. No. is 8 : 4.
- **Antifluorite Structure :** Anions have *ccp* arrangement and cations occupy all the tetrahedral voids. C. No. is 4 : 8. For example, Na_2O.
- **Density** of the crystal is related to edge length and atomic mass (formula mass) by the formula :

$$d = \frac{z \times M}{a^3 \times N_A \times 10^{-30}}$$

- **For rock salt structure**

  Closest distance of approach between **cation and anion** = 1/2 Edge length = $a/2$.

- **For CsCl structure**

  Distance of closest approach between **cation and anion** $= \frac{\sqrt{3}}{2} \times$ Edge length $= \frac{\sqrt{3} . a}{2}$.

- **In silicates** the basic unit is SiO_4^{4-} tetrahedron. The oxidation state of silicon in silicates is + 4.

  Asbestos is a chain silicate, clay is sheet silicate and quartz is an example framework silicate.
- **Point Defects :** The defects caused by missing or misplaced atoms or ions in the crystal.
- **Schottky, Frenkel and Interstitial defects** are stoichiometric defects.

  The conductivity of **semiconductors** increases with increase in temperature while that of **conductors** decreases with increase in temperature.
- **Diamagnetic Substances :** The substances that are weakly repelled by magnetic field. They have all their electrons paired.

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- **Paramagnetic Substances :** The substances that are weakly attracted by magnetic field. They have unpaired electrons in their molecules.
- **Ferromagnetic Substances :** The substances that are strongly attracted by magnetic field. For example, CrO_2, iron, cobalt and nickel.
- **Piezoelectric Effect :** Generation of electric current by applying pressure on a crystal.
- **Transition temperature :** The temperature at which a substance starts behaving as super-conductor.

EXERCISE

VERY SHORT-ANSWER QUESTIONS
(1 Mark)

1. Explain why uncharged atoms or molecules never crystallize in simple cubic lattices.
2. Will hcp and ccp structure for a given element have same density ?
3. In an alloy of gold and cadmium if gold crystallises in cubic structure occupying the corners only and cadmium fits into edge centre voids, what is the formula of the alloy ?
4. Metallic potassium crystallizes in bcc type of lattice. How many nearest neighbours does each potassium atom have ?
5. Why ZnS does not crystallize in the NaCl structure ?
6. If silver iodide crystallizes in zinc blende structure with I^- ions forming the lattice, then what fraction of tetrahedral voids is occupied by Ag^+ ions ?
7. If three elements X, Y and O crystallize in a cubic solid lattice with X atoms at the corner, Y atoms at cube centre and O atoms at edges then what is the formula of the solid ?
8. Ice crystallises in hexagonal lattice at 0°C with a volume of 132×10^{-24} cm^3. If the density of ice at 0°C is 0.91 g/cm^3, then how many water molecules are present in the unit cell.
9. What are the number of formula units in each of the following unit cells :
   (*a*) MgO in a rock salt type (*b*) Zinc blende structure.
10. NaCl crystallises in a rock-salt structure, calculate the number of unit cells present in 1.17 g of NaCl.
11. What is the coordination number of Na^+ and Cl^- ions in NaCl structure ? ***(H.P. Board 1993)***
12. What are the types of lattice imperfections found in crystals ? ***(A.I. CBSE 1993)***
13. How is ferromagnetism different from paramagnetism ? ***(A.I. CBSE 1994)***
14. What is the effect of increasing temperature on the conductivity of semiconductors ? ***(CBSE 1994)***
15. What is the number of atoms in a metallic crystal having
    (*i*) BCC arrangement (*ii*) FCC arrangement ?
16. What is the number of formula units per unit cell for an ionic solid having zinc blende structure ?
17. Explain the term dislocation in relation to crystals.

DESCRIPTIVE QUESTIONS
(2—3 Marks)

18. What is a space lattice and what is a unit cell ? Give the various types of cubic unit cells.
19. Describe hexagonal close packing. Why is it so called ?

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20. What are the various types of interstitial voids in a close packing ?
21. Illustrate an octahedral void in the close packing of spheres. Why is it so called ?
22. Does an octahedral void in a close packing of spheres, always have same size ? Explain your answer.
23. Calculate the number of atoms in face centred cubic unit cell of a mono-atomic elementary substance.
24. A solid substance AB has rock-salt structure. What are the co-ordination numbers of A and B ? How many atoms of A and how many atoms of B are present in a unit cell ?
25. Discuss the effect of temperature and pressure on the co-ordination number in case of alkali metal halides.
26. Draw a neat diagram for sodium chloride structure and then describe it accordingly. ***(P.S.E.B. 1991)***
27. Describe the structure of wustite ($Fe_{0.95}O$) and magnetite (Fe_3O_4).
28. A solid XY has zinc blende structure. Draw a unit cell of this solid and indicate the co-ordination numbers of X and Y.
29. What is the arrangement of cations and anions in the antifluorite structure ? Give one example of the compound having this type of structure.
30. Write short notes on
    (*i*) Normal spinel structure (*ii*) Radius ratio.
31. The radii of A^+ and X^- are 95 pm and 181 pm respectively. Predict the co-ordination number of A^+.
32. Arrange the following ions in the order of decreasing ionic radii :
    (*i*) $K^+, Cl^-, S^{2-}, Ca^{2+}$ (*ii*) $O^{2-}, Se^{2-}, Te^{2-}, S^{2-}$ (*iii*) $Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}$
    (*iv*) $Li^+, Na^+, Rb^+, Cs^+, K^+$ (*v*) F^-, Br^-, Cl^-, I^-.
33. Write short notes on
    (*i*) Schottky defects (*ii*) Frenkel defects.
34. What do you understand by the '*defects*' or '*imperfections*' in the crystals ? Why are these called thermodynamic defects ?
35. Describe the various types of metal excess defects in the crystals.
36. How would you explain that
    (*i*) Non-stoichiometric NaCl is yellow (*ii*) Non-stoichiometric ZnO is yellow ?
37. What do you understand by F-centres ?
38. Explain the electrical conduction in an ionic compound having metal excess defects.
39. Explain the electrical conduction mechanism in silicon doped with
    (*i*) phosphorus (P) (*ii*) gallium (Ga).
40. How do you explain that electrical conductivity of copper decreases with increase in temperature while that of solid sodium chloride increases ?
41. Explain the terms
    (*i*) Ferromagnetic substances (*ii*) Paramagnetic substances
    (*iii*) Diamagnetic substances.
42. Describe the differences in island, chain and cyclic structures of silicates. What type of silicate structures are present in zeolites, asbestos and clay ?
43. How does amorphous silica differ from quartz ?
44. What is piezoelectricity and pyroelectricity ?
45. Write a short note on amorphous solids.
46. What are ferroelectrics and antiferroelectrics ? Give one example of each type.
47. What are the differences between crystalline and amorphous solids ?
48. What do you understand by imperfections in ionic crystals ? Name the types of imperfections which generally occur in ionic crystals.
49. Explain the dielectric properties of solids. *(H.P. Board 1993)*

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NUMERICAL PROBLEMS

50. In a crystalline solid, anions C are arranged in cubic close-packing. Cations A occupy 50% of the tetrahedral voids and cations B occupy 50% of the octahedral voids. What is the formula of the solid ?

51. In a crystalline solid anions B are arranged in cubic close-packing. Cations A are equally distributed between octahedral and tetrahedral voids. If all the octahedral voids are occupied, what is the formula of the solid ?

52. If the length of body diagonal for CsCl, which crystallises into a cubic structure with Cl^- ions at the corners and Cs^+ ions at the centre of unit cell, is 7 Å and the radius of Cs^+ ion is 1.69 Å what is the radius of Cl^- ion.

53. For a cubic crystal, the face diagonal is 3.50 Å, calculate the face length.

54. If the length of cubic unit cell of the f.c.c. lattice of metallic gold is 407 pm, then calculate the density of gold in solid state ? Atomic mass of gold is 197.0.

55. The edge of f.c.c. unit cell of platinum is 392 pm and density is 21.5 g/cm^3, evaluate the Avogadro's number.

56. If radius of an atom of an element is 150 pm and it crystallises as face centred cubic lattice, then what is the face length of the unit cell ?

57. PbS has sodium chloride structure. If the shortest distance between Pb^{+2} ions and S^{2-} ion is 297 pm then calculate (*i*) the edge length of unit cell and (*ii*) density in g/cm^3.

58. If the radius of Mg^{+2} ion, Cs^+ ion, O^{2-} ion, S^{2-} ion and Cl^- ion are 0.65 Å, 1.69 Å, 1.40 Å, 1.84 Å and 1.81 Å respectively then calculate the coordination number of cation in crystals MgO, MgS and CsCl.

59. Metallic copper crystallizes in b.c.c. lattice. If the length of cubic unit cell is 362 pm, then calculate the closest distance between two copper atoms. Also calculate the density of crystalline copper.

60. Copper crystal has a face centred cubic lattice structure. Its edge length is 360 pm. What is the distance of closest approach for two copper atoms ?

61. The density of CsBr, which has a CsCl (BCC) structure, is 4.4 g cm^{-3}. The unit cell edge length is 400 pm. Calculate the interionic distance in crystal of CsBr. ($N = 6.023 \times 10^{23}$ mol^{-1}, Atomic masses : Cs = 133, Br = 80). *(CBSE 1993)*

62. An element (atomic mass = 60) having face centred cubic structure has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell ? (Avogadro's constant, $N = 6.02 \times 10^{23}$ mol^{-1}). *[A.I. CBSE (1) 1994]*

63. The unit cell of an element of atomic mass 108 and density 10.5 g cm^{-3} is a cube with edge length 409 pm. Find the structure of the crystal lattice (Simple cubic, FCC or BCC). Avogadro's constant = 6.023×10^{23} mol^{-1}. *[A.I. CBSE (1) 1995]*

64. Sodium metal crystallises in body centred cubic lattice with the cell edge = 4.29 Å. What is the radius of sodium atom ? *(I.I.T. 1994)*

65. The composition of a sample of *wustite* is $Fe_{0.93}O_{1.00}$. What percentage of the iron is present in the form of Fe (III) ? *(I.I.T. 1994)*

66. A body centred cubic element having density 10.3 g cm^{-3} has a cell-edge of 314 pm. Calculate the atomic mass of the element. (Avogadro's constant, $N_A = 6.023 \times 10^{23}$ mol^{-1}) *[A.I. CBSE (2) 1995]*

67. Sodium chloride crystallises in face-centred cubic (FCC) structure. Its density is 2.165 g cm^{-3}. If the distance between Na^+ and its nearest Cl^- is 281 pm, find out the Avogadro's number. (Na = 23 g mol^{-1}, Cl = 35.44 g mol^{-1}). *[CBSE (1) 1994]*

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FOR THE COMPETITIVE EXAMS

MULTIPLE CHOICE QUESTIONS

In each of the questions given below select the correct answer :

1. The number of atoms in a body centred cubic unit cell of a monoatomic elementary substance is equal to
(*a*) one (*b*) two (*c*) three (*d*) four.
2. An atom at the edge centre of a unit cell makes ..... contribution to a particular unit cell.
(*a*) 1/2 (*b*) 1/4 (*c*) 1 (*d*) 1/8.
3. In a cubic close packing of spheres in three dimensions, the co-ordination number of each sphere is
(*a*) 6 (*b*) 9 (*c*) 3 (*d*) 12.
4. Radius of an octahedral void relative to the radius of the spheres in a close packing is
(*a*) 1.414 (*b*) 0.225 (*c*) 1.225 (*d*) 0.414.
5. Among the following types of voids, which is the largest
(*a*) triangular (*b*) cubic (*c*) tetrahedral (*d*) octahedral.
6. Edge length of a cube is 400 pm. Its body diagonal would be
(*a*) 600 pm (*b*) 566 pm (*c*) 693 pm (*d*) 500 pm.
7. In antifluorite structure co-ordination number of anion is
(*a*) 4 (*b*) 6 (*c*) 8 (*d*) 12.
8. In the rock-salt structure, the number of formula units per unit cell is equal to
(*a*) 2 (*b*) 3 (*c*) 8 (*d*) 4.
9. In fluorite structure co-ordination number of calcium ions is .....
(*a*) 4 (*b*) 6 (*c*) 8 (*d*) 3.
10. In antifluorite structure the negative ions
(*a*) occupy tetrahedral voids (*b*) occupy octahedral voids
(*c*) are arranged in ccp (*d*) are arranged in hcp.
11. Which of the following ions has smallest ionic radius ?
(*a*) Na^+ (*b*) Mg^+ (*c*) Al^+ (*d*) Si^+.
12. Which of the following ions has the largest ionic radius ?
(*a*) Na^+ (*b*) Mg^{2+} (*c*) Al^{3+} (*d*) Si^{4+}.
13. In a HCP lattice the number of nearest neighbours for a given lattice point is
(*a*) 6 (*b*) 4 (*c*) 8 (*d*) 12.
14. Density of a crystal is given by the formula
(*a*) $\frac{a^3M}{ZN_0}$ (*b*) $\frac{N_0M}{Za^3}$ (*c*) $\frac{ZM}{a^3N_0}$ (*d*) $\frac{a^3N_0}{Z \times M}$.
15. General formula of amphiboles is
(*a*) $(SiO_3^{2-})_n$ (*b*) $(Si_2O_5^{2-})_n$ (*c*) $(Si_4O_{11}^{6-})_n$ (*d*) $(SiO_2)_n$.
16. In a compound oxide ions have CCP arrangement. Cations A are present in one-eighth of the tetrahedral holes and cations B occupy half the octahedral holes. The simplest formula of the compound is
(*a*) AB_2O_4 (*b*) A_2BO_4 (*c*) ABO_2 (*d*) ABO_4.

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17. In a compound XY_2O_4, oxide ions are arranged in CCP and cations X are present in octahedral voids. Cations Y are equally distributed between octahedral and tetrahedral voids. The fraction of the octahedral voids occupied is
(a) 1/2 (b) 1/4 (c) 1/8 (d) 1/6.

18. The electrical conductivity of the semiconductors is of the order of
(a) 10^{-9}—10^{2} Ohm^{-1} cm^{-1} (b) 10^{-9}—10^{6} Ohm^{-1} cm^{-1}
(c) 10^{6}—10^{8} Ohm^{-1} cm^{-1} (d) 10^{-12} Ohm^{-1} cm^{-1}.

19. Which of the following statements is not true ?
(a) Conductivity of semiconductors increases with increase in temperature
(b) Pure ionic solids are insulators
(c) NaCl is a diamagnetic compound (d) TiO_2 is a paramagnetic substance.

20. Which of the following is an example of paramagnetic solid ?
(a) NaCl (b) KF (c) TiO_2 (d) CuO.

21. In antifluorite structure, what percentage of the tetrahedral voids is occupied by anions ?
(a) 0% (b) 50% (c) 100% (d) 25%.

22. A metal M has FCC arrangement and edge length of the unit cell is 400 pm. The atomic radius of 'M' is
(a) 100 pm (b) 200 pm (c) 141 pm (d) 173 pm.

23. In a solid, oxide ions are arranged in CCP. The cations A occupy one-sixth of the tetrahedral voids and cations B occupy one-third of the octahedral voids. The formula of the compound is
(a) ABO_3 (b) AB_2O_3 (c) A_2BO_3 (d) $A_2B_2O_3$.

24. In zinc blende structure, the percentage of tetrahedral voids occupied by Zn^{2+} ions is
(a) 25% (b) 50% (c) 100% (d) None of these.

25. In a metal M having BCC arrangement, edge length of the unit cell is 400 pm. The atomic radius of 'M' is
(a) 200 pm (b) 100 pm (c) 173 pm (d) 141 pm.

26. In a compound, oxide have HCP arrangement and the cations M occupy two-third octahedral voids. The formula of the compound is
(a) M_3O (b) M_3O_2 (c) M_2O_3 (d) M_3O_4.

27. In rock salt structure, what percentage of the octahedral voids are occupied by cations ?
(a) 50% (b) 100% (c) 25% (d) 33%.

28. Which of the following is a ferromagentic compound ?
(a) Fe_2O_3 (b) Fe_3O_4 (c) Cr_2O_3 (d) CrO_2.

29. Which of the following is a diamagnetic compound ?
(a) MnO_2 (b) V_2O_5 (c) TiO (d) Fe_2O_3.

30. Quartz is an example of
(a) chain silicate (b) infinite sheet silicate (c) framework silicate (d) cyclic silicate.

31. Which of the following is an amorphous solid ?
(a) NaCl (b) CaF_2 (c) glass (d) CsCl.

32. The electrical conductivity of the metals is of the order of .....
(a) 10^{12} ohm^{-1} cm^{-1} (b) 10^{8} ohm^{-1} cm^{-1} (c) 10^{2} ohm^{-1} cm^{-1} (d) 10^{-6} ohm^{-1} cm^{-1}

33. The material used in the solar cells contains
(a) Cs (b) Si (c) Sn (d) Ti. *(I.I.T. 1993)*

34. The number of unit cells in 936 amu of sodium chlorides is
(a) 4 (b) 16 (c) 8 (d) $4N_0$.

35. A solid has a structure in which W atoms are located at the corners of the cubic lattice, O atoms at the centre of the edges and Na atom at the centre of the cube. The formula of the compound is
(a) $NaWO_2$ (b) Na_2WO_3 (c) $NaWO_3$ (d) $NaWO_4$.
(CEET Kurukshetra 1996)

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ASSERTION—REASON TYPE QUESTIONS

The following questions consist of two statements one labelled as ***Assertion* A** and the other ***Reason* R**. Examine both the statements carefully and mark the correct choice according to the instructions given below.

(*a*) if both A and R are correct and R is correct reason of A

(*b*) if both A and R are correct but R is not correct reason of A

(*c*) if A is correct R is wrong

(*d*) if A is wrong R is correct.

36. ***Assertion* A :** Schottky defect is generally shown by the compounds with high co-ordination number.

***Reason* R :** In Schottky defect equal number of anions and cations are missing from their lattice sites.

(*a*) (*b*) (*c*) (*d*)

37. ***Assertion* A :** In sodium chloride crystal, the Na^+ ion occupies the octahedral void while Cl^- ions occupy the vertices of octahedron.

***Reason* R :** The radius ratio $Na^+ : Cl^-$ lies between 0.4 to 0.7.

(*a*) (*b*) (*c*) (*d*)

38. ***Assertion* A :** Glass belongs to the category of ionic solid.

***Reason* R :** Glass is supercooled liquid.

(*a*) (*b*) (*c*) (*d*)

39. ***Assertion* A :** In CsCl crystal, the co-ordination number of Cs^+ ion is 8.

***Reason* R :** Cl^- ion in CsCl adopt bcc type of packing.

(*a*) (*b*) (*c*) (*d*)

40. ***Assertion* A :** For compounds exhibiting Frenkel defect, the density remains unaltered.

***Reason* R :** Doping of group 14 element with suitable element of group 13 produces *p*-type of semi-conductors.

(*a*) (*b*) (*c*) (*d*)

41. ***Assertion* A :** The electrical conductivity of metals is due to Schottky type defects.

***Reason* R :** Fool's Gold refers to some samples of iron pyrites mineral.

(*a*) (*b*) (*c*) (*d*)

FILL IN THE BLANKS

1. Dry ice is an example of ..... solid.
2. In diamond interparticle forces are .....
3. In *hcp* arrangement of spheres, the coordination number is .....
4. In *ccp* arrangement of atoms, ... per cent of the available space remains vacant.
5. In *bcc* arrangement of atoms, ... per cent of the available space is occupied by atoms.
6. In rock-salt structure ..... per cent of the octahedral voids are occupied by cations.
7. If the radius ratio r^+/r^- is 0.325, the cation would most probably be present in a/an ..... void.
8. In CsCl structure the cations are present in ..... voids.
9. In fluorite structure, the coordination number of cations is .....
10. Glass is an example of ..... solids.
11. The conductivity of semi-conductors ..... with the increase in temperature.
12. The conduction through electrons is called ..... conduction.

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13. The number of formula units in a CsCl unit cel' ' equal to .....
14. The co-ordination number of Na^+ in rock-salt structure is .....
15. In fluorite structure positive ions are arranged in .....
16. If the radius ratio (r^+/r^-) is in the range 0.414—0.732, the compound AB is likely to have ..... structure.
17. An atom at the corner of a unit cell makes ..... contribution to a particular unit cell.
18. In zinc blende structure, ... have CCP arrangement whereas ..... are present in ..... voids.
19. In antifluorite structure, cations are present in ..... voids.
20. The number of formula units per unit cell in fluorite structure is .....

TRUE/FALSE STATEMENTS

State whether the following statements are true or false :

1. Na_2O has antifluorite structure.
2. S^{2-} ion in zinc blende structure has a co-ordination number of six.
3. Spinel is a mineral having formula $MgAl_2O_4$.
4. A compound having radius ratio (r_+/r_-) in the range 0.732—1 generally has CsCl structure.
5. Na^+, K^+ and Rb^+ are isoelectronic ions.
6. NaCl is a paramagnetic substance.
7. Diamond is an example of atomic solids.
8. Orthorhombic unit cell has the least symmetry.
9. Cubic unit cell has the highest symmetry.
10. In fluorite structure 50% of the tetrahedral voids are occupied by anions.
11. In zinc blende structure coordination number of cation as well as anion is four.
12. Among the three types of arrangement, *hcp*, *ccp* and *bcc*, the most efficient packing arrangement is *bcc*.
13. Schottky defects disturb the ratio of cations and anions in the compound.
14. If the radius ratio r_+/r_- is in the range 0.225—0.414 the cation prefers to be present in an octahedral void.
15. In rock-salt structure, the number of formula units per unit cell is four.
16. An atom present at the corner of a unit cell contributes one-fourth to a particular unit cell.

MATCHING TYPE QUESTIONS

Match the items of Column A to those given in Colum B :

Column A	Column B
1. Hexagonal close packing	1. Co-ordination number of 8
2. Inverse spinel structure	2. Na_2O
3. Antifluorite structure	3. $ZnFe_2O_4$
4. Normal spinel structure	4. *bcc*
5. CsCl crystal	5. Fe_3O_4
6. 68% occupancy of space	6. ABAB type of close packing
7. Metallic crystal	7. Diamond
8. Covalent crystals	8. Malleable and ductile.

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HINTS/ANSWERS

REVIEW PROBLEMS

2.1. 3.56 g cm^{-3} **2.2.** 578 pm **2.3.** 537 pm **2.4.** 4 **2.5.** 6.09×10^{23}
2.6. 362 pm **2.7.** 400 pm **2.8.** 12.7 g cm^{-3}.

SHORT ANSWER QUESTIONS

1. It is because the uncharged atoms or molecules are closely packed to each other.

2. Yes, because in both cases co-ordination number is same and hence the packing fraction is same.

3. $AuCd_3$ **4.** 8 **6.** 50% **7.** XYO_3 **8.** 24.08×10^{23}

9. (*a*) four (*b*) four **10.** 3.01×10^{21} **11.** 6, 6

14. Conductivity of semiconductors increases with increase in temperature.

15. (*i*) 2 (*ii*) 4. **16.** 4.

DESCRIPTIVE QUESTIONS

22. No, size of the void depends upon size of the spheres constituting the close packing.

23. 4 atoms.

24. Co-ordination number of A is six and that of B is also six. There are four atoms of A and four atoms of B per unit cell.

29. In antifluorite structure anions are arranged in cubic close packing and the cations are present in all the tetrahedral voids.

31. Radius ratio $= \frac{95}{181} = 0.525$. Since the radius ratio lies in the range 0.414 – 0.732, the cation will occupy octahedral void and will have co-ordination number of six.

32. (*i*) $S^{2-} > Cl^- > K^+ > Ca^{2+}$ (*ii*) $Te^{2-} > Se^{2-} > S^{2-} > O^{2-}$ (*iii*) $Ba^{2+} > Sr^{2+} > Ca^{2+} > Mg^{2+}$
(*iv*) $Cs^+ > Rb^+ > K^+ > Na^+ > Li^+$ (*v*) $I^- > Br^- > Cl^- > F^-$.

NUMERICAL PROBLEMS

50. A_2BC_2. **51.** A_2B. **52.** 1.81 Å.
53. 2.47 Å. **54.** 19.4 g cm^{-3}. **56.** 424 pm.
57. 594 pm ; 7.2 g cm^{-3}. **58.** 6, 4, 8.

59. In a BCC lattice, the two atoms at the corners of the cube do not touch each other. The two atoms which are the closest are the one at the centre of the cube and the one at the corner of the cube.

Closest distance between two copper atoms = Half the body diagonal

$$= \frac{1}{2}\sqrt{3} \times 362 = 313 \text{ pm.}$$

Density $= 4.45 \text{ g cm}^{-3}$.

60. In a face centred cubic lattice the distance of closest approach is half the face diagonal

$$= \frac{1}{2} . \sqrt{2} \times \text{Edge length} = \frac{1}{2} . \sqrt{2} \times 360 = 255 \text{ pm.}$$

61. Interionic distance in CsCl structure is equal to half the body diagonal

$$= \frac{1}{2} . \sqrt{3} \times \text{Edge length} = \frac{1}{2} \times \sqrt{3} \times 400 = 346 \text{ pm.}$$

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62. 400 pm.

63. In this case the number of atoms per unit cell comes out to be four. Therefore, the unit cell must be face centred cubic (FCC) as it has four atoms per unit cell.

64. For body centred cubic unit cell, the body diagonal is four times the radius of atom.

Body diagonal $= \sqrt{3} \times$ Edge length $= \sqrt{3} \times 4.29$ Å

Radius of atom $= \frac{1}{4} . \sqrt{3} \times 4.29$ Å $=$ **1.86 Å.**

65. In wustite some of the iron is present in Fe (II) state and some is present in Fe (III) state. From the formula, it is clear that for 100 atoms of oxygen there are 93 atoms of Fe.

Suppose x atoms are present in Fe (III) state. Then number of Fe atoms in (II) state is $(93 - x)$. Since wustite is electrically neutral, the total charge on 93 Fe ions should be equal to total charge on 100 oxide (O^{2-}) ions

$$x \times 3 + (93 - x)2 = 100 \times 2$$

$$x = 14$$

Thus, out of 93 Fe atoms, x are present as Fe (III)

The percentage of Fe atoms in Fe (III) state $= \frac{14}{93} \times 100 =$ **15.05%.**

66. 96.

67. 6.08×10^{23}

Here, edge length $= 2\,(r_{Na^+} + r_{Cl^-}) = 2 \times 281 = 562$ pm.

MULTIPLE CHOICE QUESTIONS

1. (*b*)	**2.** (*b*)	**3.** (*d*)	**4.** (*d*)	**5.** (*b*)	**6.** (*c*)
7. (*c*)	**8.** (*d*)	**9.** (*c*)	**10.** (*c*)	**11.** (*a*)	**12.** (*a*)
13. (*d*)	**14.** (*c*)	**15.** (*c*)	**16.** (*a*)	**17.** (*a*)	**18.** (*a*)
19. (*d*)	**20.** (*d*)	**21.** (*c*)	**22.** (*c*)	**23.** (*a*)	**24.** (*b*)
25. (*c*)	**26.** (*c*)	**27.** (*b*)	**28.** (*d*)	**29.** (*b*)	**30.** (*c*)
31. (*c*)	**32.** (*b*)	**33.** (*b*)	**34.** (*a*)	**35.** (*c*)	**36.** (*b*)
37. (*a*)	**38.** (*d*)	**39.** (*c*)	**40.** (*b*)	**41.** (*c*).	

FILL IN THE BLANKS

1. molecular	**2.** covalent bonds	**3.** 12
4. 26	**5.** 68	**6.** 100
7. tetrahedral	**8.** cubic	**9.** 8
10. amorphous	**11.** increases	**12.** *n*-type
13. one	**14.** six	**15.** CCP
16. rock-salt	**17.** 1/8	**18.** anions ; cations ; tetrahedral
19. tetrahedral	**20.** 4.	

TRUE/FALSE STATEMENTS

1. True	**2.** False	**3.** True	**4.** True	**5.** False	**6.** False
7. False	**8.** False	**9.** True	**10.** False	**11.** True	**12.** False
13. False	**14.** False	**15.** True	**16.** False		

MATCHING TYPE QUESTIONS

1—6 ; 2—5 ; 3—2 ; 4—3 ; 5—1 ; 6—4 ; 7—8 ; 8—7.

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3

Solutions

LEARNING OBJECTIVES

In this Unit, we shall learn

- *the types of solutions* ;
- *the different ways of expressing the concentration of a solution* ;
- *vapour pressure of solution and Raoult's law* ;
- *colligative properties* ;
- *non-ideal solutions and abnormal molecular masses.*

A **solution** *is a homogeneous mixture of two or more pure substances whose composition may be altered within certain limits.* Though the solution is homogeneous in nature, yet it retains the properties of its constituents. The substances which make up the solution are generally called its *components*. The solution of two components is referred to as *binary solution*. Similarly, the solutions of *three* and *four* components are called *ternary* and *quaternary solutions* respectively. The two components of the binary solutions are respectively called a *solvent* and a *solute*. **Solvent** is that component in the solution whose physical state is the same as that of the resulting solution while the other component is called **solute**. For solutions in which both the components have the same physical state as that of solution, the component which is in excess is called **solvent** and the other is called **solute**. For example, in case of solution of sugar and water, sugar is the solute and water is the solvent.

In this chapter, we shall limit our discussion to the solutions of non-volatile solutes in volatile liquid solvents and some of their important properties such as relative lowering of vapour pressure, elevation of boiling point, depression in freezing point and the osmotic pressure. These properties are collectively known as the *colligative properties*. Before we take up these properties, let us briefly discuss the various types of solutions.

3.1. TYPES OF SOLUTIONS

Depending upon the physical state of the solvent and solute, the solutions can be classified into nine types. These various types of solutions have been given in Table 3.1.

Table 3.1. Types of Solutions

Solvent	*Solute*	*Example*
Gas	Gas	Mixture of gases, air.
Gas	Liquid	Water vapours in air, mist.
Gas	Solid	Sublimation of a solid into a gas, smoke.
Liquid	Gas	CO_2 gas dissolved in water (aerated drinks).
Liquid	Liquid	Mixture of miscible liquids, *e.g.*, alcohol in water.
Liquid	Solid	Salt in water, sugar in water.
Solid	Gas	Adsorption of gases over metals ; hydrogen over palladium.
Solid	Liquid	Mercury in zinc, mercury in gold.
Solid	Solid	Homogeneous mixture of two or more metals (alloys), *e.g.*, copper in gold, zinc in copper.

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Among these solutions the most significant type of solutions are those which are in liquid phase and may be categorised as :

Solid in liquid solutions,

Liquid in liquid solutions and

Gas in liquid solutions.

1. Solid in Liquid Solutions

For the solid in liquid solutions the solid is referred to as solute. The *amount* of solute that is dissolved in 100 g of a solvent, to form a saturated solution at a particular temperature is called **solubility**. The solubility of a solid solute in liquid depends upon.

(*i*) Temperature

(*ii*) Nature of solute and solvent.

Cause of miscibility of solids in liquids

The basic cause of solubility of solid solute in liquid solvent can be summed up in one line, *i.e.*, "*Similia similibus solvanter*" meaning **like dissolves like** which implies that polar solvents dissolve polar solutes and non-polar solvents dissolve non-polar solutes. For example, ionic compounds like NaCl, KCl, etc., are very soluble in water but insoluble in solvents like CCl_4, CS_2, etc. Similarly, non-polar compounds such as I_2, S_8 are more soluble in CCl_4 but insoluble in water.

The solubility of ionic solids is attributed to the ion-dipole interactions. The ion-dipole interaction release energy called **solvation energy (hydration energy** in case of water solvent). Which is largly responsible for the dissolution process.

In general, $$\Delta H_{Solution} = \Delta H_{Lattice} + \Delta H_{Hydration}$$

2. Liquid in Liquid Solutions

When two liquids are mixed, the mixture may be of the following types :

(*i*) *The two components may be almost immiscible.* In this case, one of the liquids is polar while the other is of non-polar nature. For example, benzene and water.

(*ii*) *The miscibility of the component may be partial.* If the intermolecular attraction of one liquid is different from intermolecular attraction of the other, there may be a partial miscibility of the two liquids. For example, ether and water.

(*iii*) *The two components may be completely miscible.* In this case, the two liquids are of the same nature, *i.e.*, they are either polar (like alcohol and water) or non-polar (like benzene and hexane).

Cause of miscibility of liquids

(*i*) *Chemically alike liquids dissolve in one another* more freely as compared to others, for example, alkanes are miscible in all proportions with one another. Alkanes are, however, not miscible with water because they cannot form H-bonds with water molecules.

(*ii*) *Dipole-Dipole interactions* also play an important role in forming liquid solutions.

(*iii*) *Molecular sizes of liquids* which are naturally soluble, are also approximately same.

3. Gas in Liquid Solutions

Most of the gases are soluble in water to some extent. The solubility of gas in water generally depends upon the following factors :

(*i*) Nature of the gas, (*ii*) Temperature and (*iii*) Pressure.

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In general the gases which are easily liquefiable are more soluble in water. The dissolution of gas in water is exothermic process. Hence, the solubility of gas decreases with rise in temperature. The effect of pressure on the solubility of a gas is given by **Henry's law** which states that ***mass of the gas dissolved per unit volume of a liquid at particular temperature is directly proportional to the pressure of the gas above liquid at equilibrium.***

3.2. METHODS OF EXPRESSING THE CONCENTRATION OF A SOLUTION

The concentration of a solution refers to *the amount of solute present in the given quantity of solution or solvent*. The concentration of the solution may be expressed in any of the following ways :

1. Mass Percentage

Mass percentage may be defined as the *number of parts by mass of solute per hundred parts by mass of solution.*

For example, a 5% (by mass) solution of sugar in water means that 100 g of solution contain 5 g of sugar.

If W_A be the mass of solute (A) and W_B be the mass of solvent (B), then

$$\textbf{Mass percentage of A} = \frac{W_A}{W_A + W_B} \times 100 \qquad ...(3.1)$$

2. Volume Percentage

Volume percentage may be defined as the *number of parts by volume of solute per hundred parts by volume of solution.*

If V_A and V_B be volumes of component A and B, then

$$\textbf{Volume percentage of A} = \frac{V_A}{V_A + V_B} \times 100 \qquad ...(3.2)$$

For example, a 25% solution of ethyl alcohol (by volume) means that 100 cm^3 of the solution contain 25 cm^3 of ethyl alcohol and 75 cm^3 of water.

3. Normality

Normality of a solution is defined as the *number of gram equivalents of the solute dissolved per litre of the solution.* It is represented by N.

Mathematically,

$$\text{Normality (N)} = \frac{\text{Gram-equivalents of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Mass of solute in grams}}{(\text{Gm. Eq. Mass of solute}) \times (\text{Volume of solution (L)})}$$

or

$$N = \frac{W_B\,(g)}{GEM \times V_{(L)}} \text{ or } \frac{W_B\,(g) \times 1000}{GEM \times V_{(ml)}} \qquad ...(3.3)$$

A solution having normality equal to one is called a *normal solution*. Such a solution contains one gram equivalent of solute per litre of solution. A *decinormal* solution contains 1/10 gram equivalents of solute per litre of solution. Similarly, a *semi-normal* solution contains $\frac{1}{2}$ gram equivalents and a *centinormal* solution contains 1/100 gram equivalents per litre of solution.

4. Molarity

Molarity of a solution is defined as *the number of gram-moles of the solute dissolved per litre of the solution.* It is represented by M.

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Mathematically,

$$\text{Molarity (M)} = \frac{\text{Gram-moles of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Mass of solute in grams}}{(\text{GMM of solute}) \times \text{Volume of soln. (L)}}$$

or

$$\mathbf{M = \frac{W_B\,(g)}{GMM \times V_{(L)}} \text{ or } \frac{W_B\,(g) \times 1000}{GMM \times V_{(ml)}}} \quad ...(3.4)$$

A solution having molarity one is called *molar solution.* Such a solution contains one mole of solute per litre of solution. Molarity is expressed in units of *moles per litre* or *moles per* dm^3. It may be noted that ***both normality as well as molarity of a solution change with change in temperature.***

5. Molality

Molality of a solution may be defined as *the number of gram moles of the solute dissolved in 1000 gm (1 kg) of the solvent.* It is represented by *m.*

Mathematically,

$$\text{Molality } (m) = \frac{\text{Gram moles of solute}}{\text{Mass of solvent (kg)}}$$

$$= \frac{\text{Mass of solute (g)}}{(\text{GMM of solute}) \times (\text{Mass of solvent (kg)})}$$

or

$$\mathbf{m = \frac{W_B\,(g)}{GMM \times W_A\,(kg)} \text{ or } \frac{W_B\,(g) \times 1000}{GMM \times W_A\,(g)}} \quad ...(3.5)$$

A solution containing one mole of solute pre 1000 g of solvent has molality equal to one and is called a *molal solution.* Molality is expressed in units of moles per kilogram (mol kg^{-1}). The ***molality of a solution does not change with temperature.***

SOME IMPORTANT FORMULAE

Some very significant formulae about different modes of concentrations of solution are being given below for making the calculations easy.

1. Relationship between Molarity and Normality

The normality (N) and molarity (M) of a solution are related as follows :

$$\boxed{\textit{Molarity} \times \textit{Mol. mass (solute)} = \textit{Normality} \times \textit{Eq. mass (solute)}}$$

For **Acids** ; *Normality = Basicity × Molarity*

For **Bases** ; *Normality = Acidity × Molarity*

Basicity is the number of H^+ ions furnished by each molecule of acid in solution.

Acidity is the number of OH^- ions furnished by each molecule of base in solution.

2. Relationship between Molarity and Mass percentage

If *p* is the mass percentage and *d* is the density of the solution the *molarity/normality* are given by :

$$\boxed{\textit{Molarity} = \frac{p \times d \times 10}{\textit{Mol. mass (solute)}}; \quad \textit{Normality} = \frac{p \times d \times 10}{\textit{Eq. mass (solute)}}}$$

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3. Relationship between Molarity and Molality. Molarity (M) and molality (m) are related to each other by the following relation where, d is the density of the solution.

$$m = \frac{100 \times M}{(100 \times d) - (M \times GMM_{solute})}$$

4. Dilution formula. If the solution of some substance is diluted by adding solvent from volume V_1 to volume V_2, then

$$M_1V_1 = M_2V_2 \qquad \text{Similarly,} \qquad N_1V_1 = N_2V_2$$

5. Molarity of a mixture. If V_1 ml of molarity M_1 is mixed with another solution of same substance with volume V_2 and molarity M_2, then molarity of the resulting mixture solution (M) can be obtained from

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

6. Mole Fraction

Mole fraction may be defined as the *ratio of number of moles of one component to the total number of moles of all the components (solvent and solute) present in the solution.* It is denoted by the letter X. Let us suppose that a solution contains the components A and B and suppose that W_A g of A and W_B g of B are present in it.

Number of moles of A is given by, $n_A = \frac{W_A}{M_A}$

and the number of moles of B is given by, $n_B = \frac{W_B}{M_B}$

where M_A and M_B are molecular masses of A and B respectively.

Total number of moles of A and B = $n_A + n_B$

Mole fraction of A, $X_A = \frac{n_A}{n_A + n_B}$

Mole fraction of B, $X_B = \frac{n_B}{n_A + n_B}$

The sum of mole fractions of all the components in the solution is always **one.**

$$X_A + X_B = \frac{n_A}{n_A + n_B} + \frac{n_B}{n_A + n_B} = 1.$$

Thus, if we know the mole fraction of one component *of a binary solution*, the mole fraction of the other can be calculated. It may be noted that the ***mole fraction is independent of the temperature.***

7. Formality

Formality of a solution may be defined as *the number of gram formula masses of the ionic solute dissolved per litre of the solution.* It is represented by F.

Mathematically,

$$\text{Formality (F)} = \frac{\text{Number of gram formula masses of solute}}{\text{Volume of solution in litres}}$$

$$= \frac{\text{Mass of ionic solute (g)}}{(\text{Gm. formula mass of solute}) \times (\text{Volume of soln. (L)})}$$

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Thus, $$F = \frac{W_B\,(g)}{GFM \times V_{(L)}} \text{ or } \frac{W_B\,(g) \times 1000}{GFM \times V_{(ml)}} \quad ...(3.6)$$

Commonly, the term formality is used to express the concentration of the ionic solids which do not exist as molecules but exist as network of ions. A solution containing one gram formula mass of solute per litre of the solution has formality equal to one and is called *formal solution.* It may be mentioned here that the ***formality of a solution changes with change in temperature.***

8. Parts per million (ppm)

When a solute is present in very minute amounts, its concentration is expressed in parts per million. It may be defined as *the number of parts by mass of solute per million parts by mass of the solution.* It is abbreviated as ppm.

$$\text{Parts per million (ppm)} = \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^6.$$

$$\textbf{ppm} = \frac{W_B}{W_A + W_B} \times 10^6 \quad ...(3.7)$$

This mode of concentration is generally used to express very low concentrations such as hardness of water or concentration of Cl_2 in public supply of potable water.

Example 3.1. *Calculate the concentration of a solution that is obtained by mixing 300 g of 25% solution of NH_4NO_3 with 150 g of a 40% solution of NH_4NO_3.*

Solution. Total mass of solution = 150 + 300 = 450 g

Amount of solute present in 300 g of 25% solution = $300 \times \frac{25}{100} = 75$ g

Similarly, amount of solute present in 150 g of 40% solution = $150 \times \frac{40}{100} = 60$ g

Total mass of solute = 75 + 60 = 135 g

Concentration of solution (in %age) $= \frac{\text{Mass of solute in gm}}{\text{Mass of solution in gm}} \times 100$

$= \frac{135}{450} \times 100 = \mathbf{30\%}.$

Example 3.2. *Calculate the molarity and normality of a solution containing 40 g of NaOH dissolved in two litres of the solution.*

Solution. Step I. *To calculate the mass of NaOH present in 1 litre of the solution.*

Amount of NaOH present in 2 litres of the solution = 40 g

$\therefore$ Amount of NaOH present in 1 litre of the solution $= \frac{40}{2} = 20$ g.

Step II. *To calculate the normality and molarity of the solution.*

Molecular mass of NaOH = 40.

Equivalent mass of NaOH $= \frac{40}{1} = 40$

$$\text{Normality} = \frac{\text{Mass of solute in grams per litre}}{\text{Equivalent mass of the solute}} = \frac{20}{40} = \mathbf{0.5\ N.}$$

$$\text{Molarity} = \frac{\text{Mass of solute in grams per litre}}{\text{Molecular mass of the solute}} = \frac{20}{40} = \mathbf{0.5.\ M.}$$

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Example 3.3. *Concentrated sulphuric acid in a bottle is labelled as 49% H_2SO_4 by mass and its density is 1.5 g cm^{-3}. Calculate (i) molarity, (ii) normality, and (iii) molality of H_2SO_4.*

Solution. A 49% of H_2SO_4 solution means 49 g of it is present in 100 g of the solution.

Step I. *To calculate the molarity of the solution.*

Molecular mass of H_2SO_4 = 98

Volume of 100 g of H_2SO_4 $= \frac{\text{Mass}}{\text{Density}} = \frac{100}{1.5} = 66.6$ ml.

Now, the amount of H_2SO_4 in 66.6 ml of solution = 49 g

∴ Amount of H_2SO_4 in one litre of the solution $= \frac{49}{66.6} \times 1000$ g

Molarity $= \frac{\text{Mass of solute in grams per litre}}{\text{Molecular mass of solute}}$

$= \frac{49 \times 1000}{66.6 \times 98} = 7.5$

∴ Molarity of the solution = **7.5.**

Step II. *To calculate the normality of the solution.*

Equivalent mass of H_2SO_4 $= \frac{\text{Molecular mass}}{2} = \frac{98}{2} = 49$

Normality $= \frac{\text{Mass of solute in grams per litre}}{\text{Eq. mass of solute}} = \frac{49 \times 1000}{66.6 \times 49} = 15$

So, normality of the solution = **15.**

Step III. *To calculate the molality of the solution.*

Mass of H_2SO_4 in 100 g of the solution = 49 g

∴ Mass of water present = 100 – 49 = 51 g

Amount of H_2SO_4 in 51 g of water = 49 g

∴ Amount of H_2SO_4 in 1000 g of water $= \frac{49}{51} \times 1000$

Molality $= \frac{\text{Mass of the solute per kg of solvent}}{\text{Molecular mass of the solute}}$

$= \frac{49 \times 1000}{51 \times 98} = 9.8$ mol kg^{-1}

∴ Molality of the solution = **9.8 mol kg^{-1}.**

Example 3.4. *Calculate the molarity of NaOH solution obtained by dissolving 2 g of NaOH in 50 ml of its solution.*

Solution. 50 ml of NaOH solution contains NaOH = 2 g

100 ml of NaOH solution will contain NaOH $= \frac{2}{50} \times 1000 = 40$ g

Number of moles in 40 g of NaOH $= \frac{40}{40} = 1$ mole

∴ Molarity of the solution = **1 M.**

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Example 3.5. *Calculate the amount of oxalic acid* $[(COOH)_2.2H_2O]$ *in grams that is required to obtain 250 ml of a semi-molar solution.*

Solution. Molecular mass of oxalic acid = 126

1000 ml of 1 M oxalic acid require oxalic acid = 126 g

$\therefore$ 250 ml of 1 M oxalic acid will require oxalic acid = $\frac{126}{1000} \times 250 = 31.5$ g

Hence 250 ml of $\frac{M}{2}$ oxalic acid will require oxalic acid = $31.5 \times \frac{1}{2} = 15.75$ g

$\therefore$ Mass of oxalic acid required = **15.75 g.**

Example 3.6. *Calculate the mole fraction of ethanol and water in a sample of rectified spirit which contains 46 per cent of ethanol by mass.*

Solution. Let the total mass of solution = 100 g

Mass of ethanol = 46 g

Mass of water = 54 g

Molar mass of water = 18 g

Molar mass of ethanol = 46 g

Moles of ethanol $= \frac{46}{46} = 1$

Moles of water $= \frac{54}{18} = 3$

Total number of moles = 1 + 3 = 4

Mole fraction of water $= \frac{3}{4} =$ **0.75**

Mole fraction of ethanol $= \frac{1}{4} =$ **0.25.**

Example 3.7. *Calculate the resulting molarity of the solution that is obtained by adding 5 g of NaOH to 200 ml of* $\frac{M}{4}$ *NaOH solution (density = 1.05 g cm*$^{-3}$*). The density of resulting solution is 1.08 g cm*$^{-3}$*.*

Solution. The mass of 200 mol of $\frac{M}{4}$ NaOH = 200 × 1.05 = 210.0 g

1000 ml of 1 M NaOH contains NaOH = 40 g

$\therefore$ 200 ml of 1 M NaOH contains NaOH $= \frac{40}{1000} \times 200$ g

Hence 200 ml of $\frac{M}{4}$ NaOH contains NaOH $= \frac{40}{1000} \times \frac{200}{4} =$ **2 g**

Amount of NaOH added = 5 g

Total mass of NaOH in solution = 5 + 2 = 7 g

Total mass of resulting solution = 210 + 5.0 = 215 g

Now volume of 215 g of new solution $= \frac{215}{\text{density}} = \frac{215}{1.08} = 199.0$ ml

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Molarity of new solution $= \frac{7}{199} \times \frac{1000}{40} = \mathbf{0.88\ M.}$

Example 3.8. *4.0 g of NaOH are contained in one decilitre of solution. Calculate the following :*

(i) Mole fraction of NaOH *(ii) Molarity of NaOH*

(iii) Molarity of NaOH (Density of solution = 1.038 g/cm^3).

Solution. Step I. *To calculate the mole fraction of NaOH*

Mass of 100 cm^3 of solution $= 1.038 \times 100 = 103.8$ g

Mass of NaOH $= 4.0$ g

Mass of water $= 103.8 - 4.0 = 99.8$ g

$\therefore$ No. of moles of NaOH (n_A) $= \frac{4.0}{40} = 0.1$ mole

No. of moles of water (n_B) $= \frac{99.8}{18} = 5.54$ mole

$\therefore$ Mole fraction of NaOH, $X_A = \frac{n_A}{n_A + n_B} = \frac{0.1}{0.1 + 5.54} = \mathbf{0.018.}$

Step II. *To calculate the molarity of NaOH (M)*

Molarity of the solution $= \frac{\text{Mass of NaOH per litre of solution}}{\text{Molecular mass of NaOH}}$

$= \frac{40}{40} = \mathbf{1\ M.}$

Step III. *To calculate the molality of NaOH*

Mass of NaOH in 99.8 g of H_2O $= 4.0$ g

Mass of NaOH in 1000 g of H_2O. $= \frac{4.0}{99.8} \times 1000 = 40.08$ g

$\therefore$ Molality of the solution $= \frac{\text{Mass of NaOH per 1000 g of water}}{\text{Molecular mass of NaOH}}$

$= \frac{40.08}{40} = \mathbf{1.002\ mol\ kg^{-1}.}$

Example 3.9. *You are provided with one litre each of 0.5 M NaOH and 0.25 M NaOH solutions. What maximum volume of 0.30 M NaOH can be obtained from these solutions without using water at all ?*

Solution. In order get maximum volume of 0.3 M NaOH, the whole volume, *i.e.*, 1 L of 0.25 M NaOH will be used.

Let the volume of 0.5 M needed be $= x$ L

$\therefore$ Total volume of resulting solution $= (1 + x)$ L

Now, molarity of resulting mixture solution is given by

$$M = \frac{M_1V_1 + M_2V_2}{V_1 + V_2}$$

or $$0.3 = \frac{0.25 \times 1 + 0.5 \times x}{(1 + x)} \quad \text{or} \quad x = 0.25\ \text{L}$$

$\therefore$ **Maximum volume obtained = 1 + 0.25 = 1.25 L.**

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Example 3.10. *How much volume of 10 M HCl should be diluted with water to prepare 2.00 L of 5 M HCl ?*

Solution. In dilution, the following equation is applicable :

$$\underset{10\text{ M HCl}}{M_1V_1} = \underset{5\text{ M HCl}}{M_2V_2}$$

$$10 \times V_1 = 5 \times 2.00$$

$$V_1 = \frac{5 \times 2.00}{10} \text{ L} = \mathbf{1.00\ L.}$$

Example 3.11. *Commercially available concentrated hydrochloric acid contains 38% HCl by mass and has density 1.19 g cm^{-3}. What is the molarity of this solution ?*

Solution. Mass of 1000 cm^3 (1.0 L) of commercial HCl

$$= 1000 \times 1.19 = 1190 \text{ g}$$

Mass of HCl in 1190 g (1000 cm^3) of the solution

$$= \frac{1190 \times 38}{100} = 452.2 \text{ g}$$

Molar mass of HCl $= 36.5$ g

452.2 g of HCl $= \frac{452.2}{36.5}$ moles of HCl = 12.4 moles of HCl

$\therefore$ 1.0 L of the commercial HCl solution contains 12.4 moles of HCl.

Hence, molarity of the commercial HCl solution is **12.4 M.**

Example 3.12. *Calculate the volume of 80% H_2SO_4 (density = 1.80 g/cc) that is required to obtain one litre of 20% H_2SO_4 (density = 1.25 g/cc).*

Solution. Molarity of 80% H_2SO_4 $= \frac{\text{Mass of } H_2SO_4}{\text{Mass of solution}} \times \frac{\text{Density of solution}}{\text{Molecular mass}} \times 1000$

$$= \frac{80}{100} \times \frac{1.80}{98} \times 1000 = \mathbf{14.7\ M}$$

Molarity of 20% H_2SO_4 $= \frac{20}{100} \times \frac{1.25}{98} \times 1000 = \mathbf{2.55\ M}$

Applying molarity equation, $M_1V_1 = M_2V_2$

$$14.7 \times V = 2.55 \times 1000$$

or Volume of 80% H_2SO_4 required $= \frac{2.55 \times 1000}{14.7} = \mathbf{173.53\ ml.}$

Example 3.13. *Sea water contains 5.8×10^{-3} g of dissolved oxygen per kilogram. Express the concentration of oxygen in sea water in parts per million.*

Solution. Part per million $= \frac{\text{Mass of solute}}{\text{Mass of solution}} \times 10^{-6} = \frac{5.8 \times 10^{-3} \text{ g}}{10^3 \text{ g}} \times 10^6 = \mathbf{5.8\ ppm.}$

Example 3.14. *Calculate the molarity of a solution of $CaCl_2$ if on chemical analysis it is found that 200 ml of $CaCl_2$ solution contains 3.01×10^{22} chloride ions. Assume that $CaCl_2$ is completely ionised in solution.*

Solution.

$$\underset{(111\text{ g})}{CaCl_2} \longrightarrow Ca^{+2} + \underset{(2 \times 6.02 \times 10^{23}\text{ ions})}{2Cl^-}$$

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$2 \times 6.02 \times 10^{23}$ chloride ions are obtained from $CaCl_2$ = 111 g

$\therefore$ 3.01×10^{22} chloride ions will be obtained from $CaCl_2$

$$= \frac{111}{2 \times 6.02 \times 10^{23}} \times 3.01 \times 10^{22} = 2.775 \text{ g}$$

Now, 200 ml of $CaCl_2$ solution contains $CaCl_2$ = 2.775 g

$\therefore$ 1000 ml of $CaCl_2$ solution contains $CaCl_2 = \frac{2.775}{200} \times 1000 = 13.875$ g

Number of moles of $CaCl_2$ in 13.875 g $= \frac{13.875}{111} = 0.125$ moles

Hence, molarity of solution = **0.125 M.**

REVIEW PROBLEMS

3.1. What is the normality of a solution containing 40 g of Na_2CO_3 dissolved in 4 litres of solution ? (Eq. mass of Na_2CO_3 = 53)

3.2. Calculate the mole fraction, molal and molar concentrations of a solution containing 20% acetic acid by mass in water. Density of the solution at 20°C is 1.026 g cm^{-3}.

3.3. If at a particular temperature, the density of a 5 M aqueous solution of a substance of molar mass 100 g is 1.289 g cm^{-3}, calculate the molality and the mole fraction.

3.4. A solution is 25% H_2O, 25% C_2H_5OH and 50% CH_3COOH by mass. Calculate the mole fraction of each component.

3.5. Find out normality and molality of a solution containing 10 g of NaOH per 250 ml of solution, density of solution is 1.1 g/ml.

3.6. What volume of 0.025 F solution of hypo ($Na_2S_2O_3.5H_2O$) contains 1.24 g of it.

3.7. 200 ml of an aqueous solution containing 8 g of KOH are mixed with 200 ml of pentimolar KOH solution. What is the molarity of the resulting solution ?

3.8. Chemical analysis of an aqueous solution of barium chloride revealed that 100 ml of solution contains 3.01×10^{22} Cl^- ions. What is the molarity of the solution ?

3.9. A sugar syrup of mass 214.2 g contains 34.2 g of sugar ($C_{12}H_{22}O_{11}$). Calculate, molality and mole fraction of sugar. *(I.I.T. J.E.E. 1988 ; H.P.S.B. 1993)*

3.10. Find the molarity and molality of a 15% solution of H_2SO_4 (density = 1.10 gm/ml and molecular mass of H_2SO_4 = 98).

3.11. Calculate the molality of potassium carbonate solution which is formed by dissolving 2.5 g of it in one litre solution. (Density of solution is 0.85 g/ml, mass number of K = 39, C = 12, O = 16). *(Pb. 1992)*

3.12. 100 cm^3 of 10 N HCl are diluted with distilled water to a volume of 2 litres. Find out the normality of the resultant solution.

3.13. Commercially available concentrated hydrobromic acid solution contains 48% HBr by mass. What is the molarity, molality of this solution ? The density is 1.50 g cm^{-3}.

3.14. An aqueous solution of certain substance has been labbled as 1 m. Find mole fraction of solvent and solute.

3.15. In an industrial town, the pollution of SO_2 in air has been reported as 10 ppm by volume. Calculate the volume of SO_2 per litre of air.

3.16. The density of 3 M aqueous solution of sodium thiosulphate is 1.25 g/ml. Calculate (*i*) mole fraction of sodium thiosulphate (*ii*) molalities of Na^+ and $S_2O_3^{2-}$ ions. *(I.I.T. J.E.E. 1985)*

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3.17. A solution to be used as *hand lotion,* is prepared by dissolving 6.40 g of methanol and 18.40 g of glycerol ($C_3H_8O_3$) in 90 g of water. Calculate the mole fraction of glycerol.

3.18. A solution was prepared by dissolving 0.4 gm-equivalent of H_2SO_4 in 55.5 moles of water at 274 K. If density of resulting solution is 1.2 g/ml. Calculate molality and molarity of the solution (Eq. mass of H_2SO_4 = 49).

3.19. On heating one litre of semi-molar HCl, 2.675 g of hydrogen chloride gas escapes out and the volume of the solution is reduced to 750 ml. Calculate. (*i*) molarity of resulting solution and (*ii*) milli moles of HCl in 100 ml of original solution.

3.20. Calculate the volume of 80% H_2SO_4 by mass with density 1.80 g cm^{-3} which is required to prepare 500 cm^3 of 20% H_2SO_4 by mass with density 1.25 g cm^{-3}.

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3.3. VAPOUR PRESSURE OF SOLUTIONS AND RAOULT'S LAW

When a liquid is taken in a beaker covered from above, a part of the liquid evaporates and its vapours fill the space available to them. The vapours formed will have a tendency to change back to the liquid state by the process of condensation. At a particular temperature, an equilibrium will be established between liquid and vapour phases.

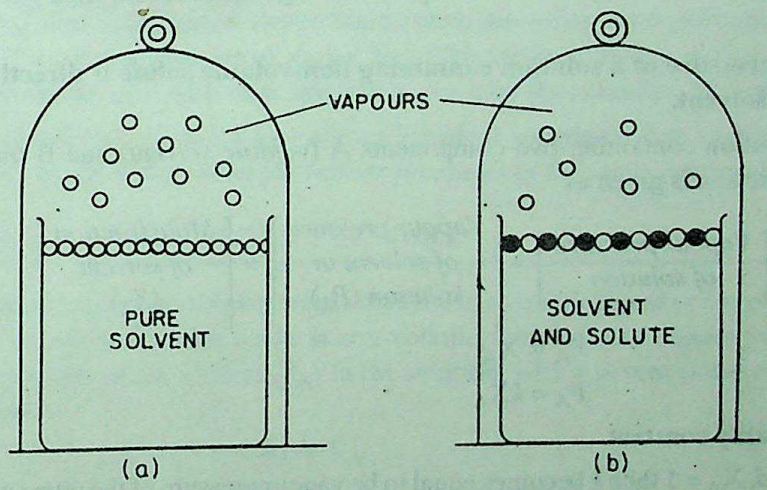

Fig. 3.1. Vapour pressure of pure liquid (*a*) and of solution (*b*).

The pressure exerted by the vapours above the liquid surface in equilibrium with the liquid at a given temperature is called **vapour pressure of the liquid.**

The vapour pressure of a liquid depends on

(*i*) *Nature of liquid*

Liquids, which have weak intermolecular forces, are volatile and have greater vapour pressure. For example, dimethyl ether has greater vapour pressure than ethyl alcohol.

(*ii*) *Temperature*

Vapour pressure increases with increase in temperature. This is due to the reason that with increase in temperature more molecules of the liquid can go into vapour phase.

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The variation of vapour pressure of a liquid with temperature is given by the following equation

$$\log \frac{P_2}{P_1} = \frac{\Delta H_{vap.}}{2.303\ R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

where, P_1 and P_2 are vapour pressures at temperature T_1 and T_2 respectively. $\Delta H_{vap.}$ is enthalpy of vaporisation of liquid and R is universal gas constant.

Vapour Pressure of the Solution

Let us consider the addition of a small amount of a non-volatile solute to the liquid (solvent) to form a solution. In such a case the vapour pressure of the solution is because of the solvent, as the solute is non-volatile. It is found that the vapour pressure of the solution is less than that of the pure solvent.

Explanation. *The lowering of vapour pressure can be explained on the basis of the surface area of the liquid from which evaporation occurs. In the case of the solution, a part of the liquid surface is occupied by solute particles, therefore, evaporation of the liquid will take place from a lesser surface area. In other words, the particles (or molecules) of the liquid will now have a* **less tendency** *to change into vapours. This shall, therefore, results in* **lowering of vapour pressure.**

Raoult' Law

Raoult carried out a series of experiments to study the vapour pressure of a number of binary solutions. On the basis of the results of the experiments, he proposed a generalisation called Raoult's law which states that.

The vapour pressure of a solution containing non-volatile solute is directly proportional to the mole fraction of the solvent.

In case of solution containing two components A (*volatile solvent*) and B (*non-volatile solute*) the vapour pressure of solution is given as

$$\begin{bmatrix} \textit{Vapour pressure} \\ \textit{of solution} \end{bmatrix} = \begin{bmatrix} \textit{Vapour pressure} \\ \textit{of solvent in} \\ \textit{solution } (P_A) \end{bmatrix} \propto \begin{bmatrix} \textit{Mole fraction} \\ \textit{of solvent} \\ (X_A) \end{bmatrix}$$

or $$P_A \propto X_A$$

or $$P_A = kX_A$$

where k is proportionality constant.

For *pure liquid*, $X_A = 1$ then k becomes equal to be vapour pressure of the pure solvent which is denoted by $P_A°$.

Thus, $$P_A = P_A° X_A$$

or $$P_{solution} = P_{pure\ solvent} \times \textit{mole fraction of solvent.}$$

In a *solution* of two **miscible volatile liquids** A and B the partial vapour pressure P_A of liquid A is proportional to its mole fraction X_A and the partial vapour pressure P_B of liquid B is proportional to its mole fraction X_B.

Thus, $$P_A \propto X_A$$

$$P_A = P_A° X_A$$

Also $$P_B \propto X_B$$

$$P_B = P_B° X_B$$

where $P_A°$ and $P_B°$ are the vapour pressures of pure components A and B respectively. This relationship is called **Raoult's law. It states that for a solution of two or more miscible volatile liquids, the partial vapour**

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pressure of each component of the solution at a particular temperature is directly proportional to its mole fraction.

According to Raoult's law a plot of P_A against X_A should give a straight line passing through $P_A°$ when $X_A = 1$ (shown by broken line I in Fig. 3.2). Similarly, a plot of P_B against X_B is a straight line passing through $P_B°$ when $X_B = 1$ (broken line II in Fig. 3.2). The total vapour pressure, P exerted by the solution is the sum of P_A and P_B as required by Dalton's law of partial pressures.

$$P = P_A + P_B$$

or

$$P = P_A°X_A + P_B°X_B \quad (\because X_A + X_B = 1)$$

$$= P_A° (1 - X_B) + P_B°X_B$$

$$= P_A° - P_A°X_B + P_B°X_B$$

$$= (P_B° - P_A°)X_B + P_A° \quad ...(3.8)$$

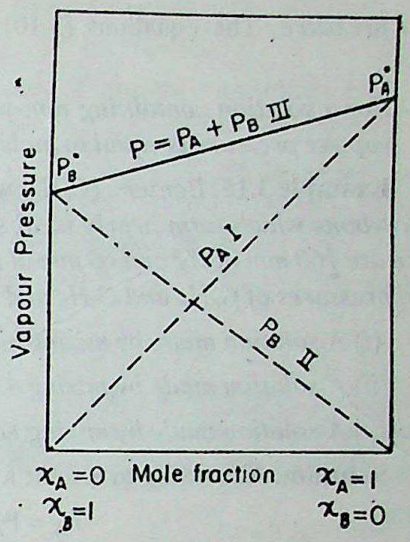

Fig. 3.2. Partial and total vapour pressure curves for solutions that follow Rault's law.

Similarly, by putting $X_B = 1 - X_A$, we can arrive at the following relation

$$P = (P_A° - P_B°)X_A + P_B° \quad ...(3.9)$$

Since $P_B°$ and $P_A°$ are constant at particular temperature, therefore, the equations (3.8) and (3.9) reveal that the total pressure, P is a linear function of X_B (or X_A). This means that plot of P *vs* X_B or P *vs* X_A should be a straight line. The variation of P with mole fraction is given by the solid line III in the graph.

The solutions which obey Raoult's law are called **ideal solutions**. *For such solutions, the vapour pressure of the solution always lies between the vapour pressures of the pure components.*

3.4. RELATIVE LOWERING OF VAPOUR PRESSURE

We have seen that if some **non-volatile solute** is added to a volatile liquid (solvent), the vapour pressure of the solvent is always lowered. Since the solute is non-volatile, therefore, the vapour pressure of the solution (P) is equal to vapour pressure of the solvent (P_A) in the solution, which in turn is directly proportional to its mole fraction in the solution.

$$P = P_A \propto X_A$$

$$P_A = P_A°X_A \quad ...(i)$$

where X_A = mole fraction of solvent

If mole fraction of solute is X_B, then

$$X_A + X_B = 1$$

or

$$X_A = 1 - X_B \quad ...(ii)$$

From Eqns. (*i*) and (*ii*),

$$P_A = P_A°(1 - X_B)$$

or

$$= P_A° - P_A°X_B$$

or

$$P_A° - P_A = P_A°X_B$$

or

$$\boxed{\frac{P_A° - P_A}{P_A°} = X_B} \quad ...(3.10)$$

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$(P_A^\circ - P_A)$ is the *lowering of vapour pressure* whereas $\left(\frac{P_A^\circ - P_A}{P_A^\circ}\right)$ is called ***relative lowering of vapour pressure***. The equations (3.10) forms the basis of an alternative statement of **Raoult's law** as follows :

For a solution containing non-volatile solute, at a particular temperature, the relative lowering of vapour pressure is equal to mole fraction of the solute.

Example 3.15. *Benzene (C_6H_6) with b. pt. 353.1 K and toluene (C_7H_8) with b. pt. 383.6 K are the two hydrocarbons which form nearly ideal solution. At 313 K, the vapour pressures of pure benzene and pure toluene are 160 mm of Hg and 60 mm of Hg respectively. Assuming an ideal solution behaviour, calculate the partial pressures of C_6H_6 and C_7H_8 and the total pressure under the following conditions :*

(i) A solution made by mixing equal number of moles of C_6H_6 and C_7H_8.

(ii) A solution made by mixing 4 moles of toluene and 1 mole of benzene.

(iii) A solution made by mixing equal masses of toluene and benzene.

Solution. According to Raoult's Law, partial vapour pressure of benzene,

$$P_A = P_A^\circ X_A$$

where P_A° is the vapour pressure of pure benzene and X_A is the mole fraction of benzene.

Partial vapour pressure of toluene $P_B = P_B^\circ X_B$

where P_B° is the vapour pressure of pure toluene and X_B is the mole fraction of toluene.

Now, let us calculate the partial pressures of the solutions.

(i) To calculate the vapour pressure of solution containing equal number of moles of benzene and toluene.

Let the number of moles of each liquid be '*a*'.

$$\therefore \quad X_A = X_B = \frac{a}{a+a} = 0.5$$

Partial vapour pressure of $C_6H_6 = P_A^\circ X_A = 160 \times 0.5 =$ **80 mm.**

Partial vapour pressure of toluene $= P_B^\circ X_B = 60 \times 0.5 =$ **30 mm.**

$\therefore$ Total vapour pressure = 80 + 30 = **110 mm of Hg.**

(ii) To calculate the vapour pressure of solution containing 4 moles of toluene and 1 mole of benzene.

$$X_A = \frac{\text{No. of moles of benzene}}{\text{Total No. of moles of benzene and toluene}}$$

$$= \frac{1}{1+4} = 0.2$$

$$X_B = 1 - 0.2 = 0.8$$

Partial vapour pressure of benzene $= P_A^\circ X_A = 160 \times 0.2 =$ **32 mm.**

Partial vapour pressure of toluene $= P_B^\circ X_B = 60 \times 0.8$ mm = **48 mm**

$\therefore$ Total vapour pressure = 48 + 32 = **80 mm of Hg.**

(iii) To calculate the vapour pressure of the solution containing equal masses of benzene and toluene.

Let the mass of benzene = mass of toluene = *m g*

$\therefore$ Moles of benzene $= \frac{m}{78}$

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and Moles of toluene $= \frac{m}{92}$

Mole fraction of benzene $X_A = \frac{\frac{m}{78}}{\frac{m}{78} + \frac{m}{92}} = 0.541$

Mole fraction of toluene $X_B = 1 - X_A = 1 - 0.541 = 0.459$

Partial vapour pressure of benzene $= P_A^\circ X_A = 160 \times 0.541 =$ **86.56 mm**

Partial vapour pressure of toluene $= 60 \times 0.459 =$ **27.54 mm**

Total vapour pressure $= 86.56 + 27.54 =$ **114.10 mm of Hg.**

Example 3.16. *The vapour pressures of ethanol and methanol are 44.5 mm and 88.7 mm Hg respectively. An ideal solution is formed at the same temperature by mixing 60 g of ethanol with 40 g of methanol. Calculate the total vapour pressure of the solution and the mole fraction of methanol in the vapour.*

(I.I.T. 1986)

Solution. Moles of ethanol $= \frac{60 \text{ g}}{46 \text{ g}} = 1.304$

Moles of methanol $= \frac{40 \text{ g}}{32 \text{ g}} = 1.250$

Mole fraction of ethanol $= \frac{1.304}{1.304 + 1.250} = 0.51$

Mole fraction of methanol $= 1 - 0.51 = 0.49$

Vapour pressure of pure ethanol,

$$P^\circ_{C_2H_5OH} = 44.5 \text{ mm}$$

Vapour pressure of pure methanol,

$$P^\circ_{CH_3OH} = 88.7 \text{ mm.}$$

Vapour pressure due to ethanol,

$$P_{C_2H_5OH} = P^\circ_{C_2H_5OH} \times 0.51$$

$$= 44.5 \text{ mm} \times 0.51 = \mathbf{22.69\ mm}$$

Vapour pressure due to methanol,

$$P_{CH_3OH} = P^\circ_{CH_3OH} \times 0.49$$

$$= 88.7 \text{ mm} \times 0.49 = \mathbf{43.46\ mm}$$

Total vapour pressure $= P_{C_2H_5OH} + P_{CH_3OH}$

$= 22.69 \text{ mm} + 43.46 \text{ mm} =$ **66.15 mm.**

Mole fraction of methanol in the vapour state

$$= \frac{P_{CH_3OH}}{\text{Total vapour pressure}}$$

$$= \frac{43.46 \text{ mm}}{66.15 \text{ mm}} = \mathbf{0.657.}$$

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Example 3.17. *A current of dry air was first passed through the bulb containing solution of A in water and then through the bulb containing pure water. The loss in mass of solution bulb is 1.949 g whereas that in pure water bulb is 0.0870 g. Calculate the mole fraction of A as well as water in solution.*

Solution. As the air passes through the solution bulb it takes up amount of vapour which is proportional to the vapour pressure of solution at the prevailing temperature. When this moist air further passes through the solvent (water) bulb, it takes up further amount of vapour which is proportional to the *difference* in the vapour pressure of pure solvent and solution.

Thus, Loss in mass of solution bulb $\propto P$

Loss in mass of solvent bulb $\propto P^\circ - P$

Total loss in mass of both the bulbs $\propto P^\circ$

According to given data $P \propto 1.949$ g ; $(P^\circ - P) \propto 0.087$ g ; $P^\circ \propto (1.949 + 0.087)$ g

Relative lowering of vapour pressure is given by

$$\frac{\Delta P}{P^\circ} = \frac{P^\circ - P}{P^\circ} = \frac{0.087}{2.036} = 0.042$$

Now according to Raoult's law

Mole fraction of A, $X_A = \frac{\Delta P}{P^\circ} = \mathbf{0.042}$

Mole fraction of H_2O, $X_{H_2O} = 1 - 0.042 = \mathbf{0.958}$.

REVIEW PROBLEMS

3.21. A liquid X has a vapour pressure 80 mm of mercury at certain temperature. The solution of liquid X and Y at the same temperature has vapour pressure 64 mm of Hg. If the solution obey's Raoult's law, calculate the mole fraction of X in the solution.

3.22. Two liquids A and B form ideal solution at 323 K. A liquid mixture containing one mole of A and two moles of B has a vapour pressure of 250 torr. If one more mole of A is added to the solution, the vapour pressure increases to 300 torr. Calculate the vapour pressures of liquids A and B at 323 K.

3.23. The mole fraction of A in the vapours in equilibrium with homogeneous mixture of liquids A and B is 0.34. The vapour pressure of pure A and B at the same temperature are 229.2 and 114.6 mm of Hg respectively. Calculate mole fraction of A in the solution.

3.24. The vapour pressure of a dilute aqueous solution of glucose ($C_6H_{12}O_6$) is 750 mm of mercury at 373 K. Calculate (*i*) molality, and (*ii*) mole fraction of the solute. *(I.I.T. 1989)*

3.25. A current of dry air was passed through two bulbs A containing solution of urea in ethanol and B containing pure ethanol. The loss in mass of bulb A was found to be 0.9675 g. But total loss of mass in A and B bulbs was 0.993 g. Calculate mole fractions of urea and ethanol in solution.

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3.5. IDEAL SOLUTIONS

An ideal solution may be defined as the solution which obeys Raoult's law over the entire range of concentration and temperature, and during the formation of which no change in enthalpy and no change in volume takes place. For example, if we mix 25 cm^3 of each of the two components to form ideal

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solution there is no evolution or absorption of heat and the final volume of solution is 50 cm^3. Thus, the conditions for an ideal solution are :

(*i*) **It should obey Raoult's law, *i.e.*, $P_A = P_A^\circ X_A$ and $P_B = P_B^\circ X_B$**

(*ii*) $\Delta H_{mixing} = 0$

(*iii*) $\Delta V_{mixing} = 0$

There is no solution which behaves strictly as an ideal solution. However, the solutions in which solvent-solvent and solute-solute interactions are almost of the same type as solvent-solute interactions, behave nearly as ideal solutions.

This type of solutions are possible if molecules of solute and solvent are almost of same size and have identical polarity. For example, solutions of following pairs almost behave as ideal solutions :

(*a*) *n*-Heptane and *n*-hexane

(*b*) Chlorobenzene and bromobenzene

(*c*) Benzene and toluene

(*d*) Ethyl bromide and ethyl iodide

(*e*) Ethylene bromide and ethylene chloride

(*f*) Carbon tetrachloride and silicon tetrachloride.

In such solutions, the interactions between molecules remain almost of the same type before and after mixing, therefore, such solutions are not accompanied by any change in enthalpy or volume, *i.e.*, $\Delta H_{mixing} = 0$ and $\Delta V_{mixing} = 0$.

For such solutions the vapour pressure of the solution is always intermediate between the vapour pressures of pure components A and B, *i.e.*, P_A° and P_B°.

It may be noted that although most of the solutions show deviations from ideal behaviour, yet they behave as ideal solutions when conc. of the solute is very low. In other words, *most of the dilute solutions behave as ideal solutions.*

3.6. NON-IDEAL SOLUTIONS

The solutions which do not obey Rault's law and are accompanied by change in enthalpy and change in volume during their formation are called non-ideal solutions. So, for non-ideal solutions the conditions are :

(*i*) $P_A \neq P_A^\circ X_A$; $P_B \neq P_B^\circ X_B$

(*ii*) $\Delta H_{mixing} \neq 0$

(*iii*) $\Delta V_{mixing} \neq 0$.

It must be noted here that for a non-ideal binary solution, none of the components follows Raoult's law.

The non-ideal solutions are further classified into two types :

(*a*) *Solutions showing positive deviations.*

(*b*) *Solutions showing negative deviations.*

Solutions with Positive Deviations

In this type of deviations, the partial vapour pressure of each component (say A and B) of solution is greater than the vapour pressure as expected according to Raoult's law. This type of deviations are shown by the solutions in which solvent-solvent and solute-solute interactions are stronger than solvent-solute interactions. Since in solution, the interactions among molecules becomes weaker, therefore, their escaping tendency increases which results in the increase in their partial vapour pressures. In such solutions total vapour pressure of the solution is also greater than the vapour pressure required according to the Raoult's law (Fig. 3.3).

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For the solutions with positive deviations there is an intermediate composition for which the vapour pressure of the solution is maximum and hence, *boiling point* is the minimum. At this composition the solution distils at constant temperature without change in composition. *A solution which distils without change in composition at a particular temperature is called* **azeotrope** or **azeotropic mixture.** The azeotrope in solutions with positive deviations is called *minimum boiling azeotrope.*

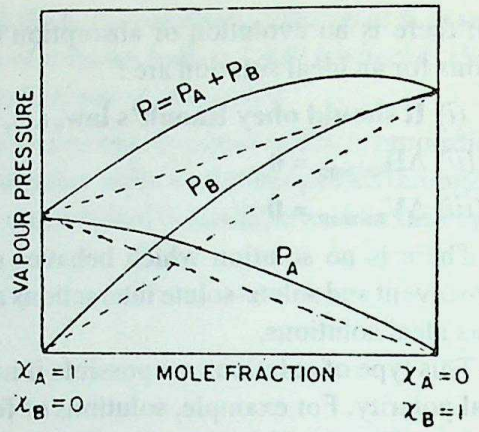
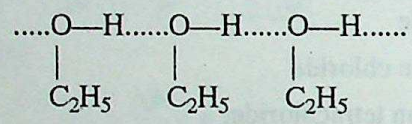


Fig. 3.3. Partial and total vapour pressure curves for solutions that show positive deviations from Rault's law.

An example of a solution with positive deviations, *i.e.*, a solution of *n*-hexane and ethanol is illustrated below to have a better understanding of such deviations. In ethanol H-bonds exist among molecules as shown below :



However, in solution, the *n*-hexane molecules come in between ethanol molecules and hence, the intermolecular forces become weaker. This results in the increase in vapour pressure. Because of decrease in the magnitude of intermolecular forces in solutions the molecules will be loosely held and hence, increase in volume takes place and hence ΔV_{mixing} = + ve. Also, process will be accompanied by absorption of energy and hence, ΔH_{mixing} = + ve.

So for the non-ideal solutions exhibiting positive deviations :

(*i*) $P_A > P_A^\circ X_A$; $P_B > P_B^\circ X_B$

(*ii*) ΔH_{mixing} = + ve.

(*iii*) ΔV_{mixing} = + ve.

Table 3.2. Non-ideal Solutions

Solutions showing positive deviations	*Solutions showing negative deviations*
$(CH_3)_2CO + CS_2$	$CH_3COOH + C_5H_5N$ (pyridine)
$(CH_3)_2CO + C_2H_5OH$	$CHCl_3 + (CH_3)_2CO$
$C_6H_6 + (CH_3)_2CO$	$CHCl_3 + C_6H_6$
$CCl_4 + C_6H_6$	$CHCl_3 + (C_2H_5)_2O$
$CCl_4 + CHCl_3$	$H_2O + HCl$
$CCl_4 + C_6H_5CH_3$	$H_2O + HNO_3$
$H_2O + CH_3OH$	$(CH_3)_2CO + C_6H_5NH_2$
$H_2O + C_2H_5OH$	
$CH_3CHO + CS_2$	
$CHCl_3 + C_2H_5OH$	

Solutions with Negative Deviations

In this type of deviations the partial vapour pressure of each component of solution is less than the vapour pressure as expected according to Raoult's law. This type of deviations are shown by the solutions in

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which solvent-solvent and solute-solute interactions are weaker that solvent-solute interactions. Since in solution the interactions among molecules become stronger, their escaping tendency decreases which results in the decrease in their partial vapour pressures. *In such solutions total vapour pressure of the solution is also less than the vapour pressure expected according to Raoult's law (Fig. 3.4).*

For the solutions with negative deviations there is an intermediate composition for which vapour pressure of the solution is minimum and hence b.pt. is maximum. At this composition the solution distils at constant temperature without the change in composition. So it is an azeotrope. The azeotrope in solutions with negative deviation is called *maximum boiling azeotrope.*

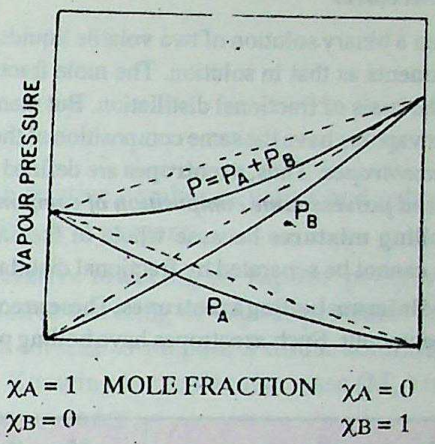
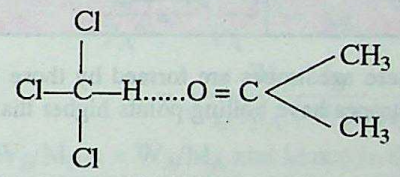


Fig. 3.4. A vapour pressure curve showing negative

An example of a solution with negative deviation is a solution of acetone and chloroform. In these components there is no hydrogen bond when they are separate, however, on mixing, hydrogen bonds are formed between acetone and chloroform molecules as shown below :



Since new attractive forces come into existence in these solutions, therefore, these solutions are accompanied by evolution of heat ($\Delta H_{mixing} = -$ ve). Also because of stronger forces of attraction among molecules in solution, the molecules come closer and hence, volume of the solution is less than the total volume of the components before mixing ($\Delta V_{mixing} = -$ ve). So for non-ideal solutions exhibiting negative deviations :

(*i*) $P_A < P_A^\circ X_A$; $P_B < P_B^\circ X_B$

(*ii*) $\Delta H_{mixing} = -$ ve

(*iii*) $\Delta V_{mixing} = -$ ve.

The various points of **differences between ideal and non-ideal** solutions have been summed up as follows :

	Ideal solutions	*Solutions with positive deviations*	*Solutions with negative deviations*
1.	A.....B interactions are similar to A.....A and B....B interactions	A.....B interactions are smaller than A.....A and B....B interactions	A.....B interactions are greater than A.....A and B....B interactions
2.	$P_A^\circ = P_A^\circ X_A$; $P_B = P_B^\circ X_B$	$P_A > P_A^\circ X_A$; $P_B > P_B^\circ X_B$	$P_A < P_A^\circ X_A$; $P_B < P_B^\circ X_B$
3.	$\Delta H_{Sol.} = 0$	$\Delta H_{Sol.} > 0$	$\Delta H_{Sol.} < 0$
4.	$\Delta V_{mix.} = 0$	$\Delta V_{mix.} > 0$	$\Delta V_{mix.} < 0$
5.	Do not form azeotrope	Exhibit minimum boiling azeotropy	Exhibit maximum boiling azeotropy

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Azeotropic Mixtures

When a binary solution of two volatile liquids is boiled, its vapours, in general, do not have the same composition of the components as that in solution. The mole fraction of the more volatile component is generally higher in vapours. This forms the basis of fractional distillation. But many binary solutions at definite compositions behave like pure liquids because their vapours have the same composition of the two components as in solution. Such solutions are called *azeotropic mixtures* or *azeotropes*. Thus, **azeotropes** are defined as ***the mixture of liquids which boil at constant temperature like a pure liquid and possess same composition of components in liquid as well as in vapour phase.*** Azeotropes are also called **constant boiling mixtures** because whole of the azeotrope changes in vapour state at constant temperature and their components cannot be separated by fractional distillation. Azeotropes are of two types as described below :

(*i*) **Minimum boiling azeotropes.** These azeotropes are formed by those liquid pairs which show positive deviation from ideal behaviour. Such azeotropes have boiling points lower than either of the components. Some examples are given below :

Components		Mass % of B	Boiling points (K)		
A	B		A	B	Azeotrope
H_2O	C_2H_5OH	95.57	373	351.3	351.1
H_2O	$C_2H_5CH_2OH$	71.69	373	370	370.72
$CHCl_3$	C_2H_5OH	67	334	351.3	332.3
$(CH_3)_2CO$	CS_2	6.8	329.25	320	312.2

(*ii*) **Maximum boiling azeotropes.** These azeotropes are formed by those liquid pairs which show negative deviations from the ideal behaviour. Such azeotropes have boiling points higher than either of the components. Some examples are given below :

Components		Mass % of B	Boiling points (K)		
A	B		A	B	Azeotrope
H_2O	HCl	20.3	373	188	383
H_2O	HNO_3	58.0	373	359	393.5
H_2O	$HClO_4$	71.6	373	383	476

3.7. COLLIGATIVE PROPERTIES

There are certain properties of dilute solutions which depend upon molar concentrations of the solute in solution but do not depend upon its nature. The properties of dilute solutions containing non-volatile solute, which depend upon relative number of solute and solvent particles but do not depend upon their nature are called colligative properties. Some of the colligative properties are :

(*i*) *Relative lowering of vapour pressure*

(*ii*) *Elevation of boiling point*

(*iii*) *Depression of freezing point*

(*iv*) *Osmotic pressure.*

1. Relative Lowering of Vapour Pressure

It has already been shown that for an ideal solution the relative lowering of vapour pressure is equal to the mole fraction of the solute (Section 3.4). This holds true even for dilute non-ideal solutions because when the concentration of solute is low, the solutions behave as ideal solutions :

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$$\frac{\Delta P}{P_A^\circ} = X_B$$

where, $\Delta P = P_A^\circ - P_A$ = lowering of vapour pressure

P_A° = vapour pressure of pure solvent.

X_B = mole fraction of solute.

Relative lowering of vapour pressure depends upon relative number of solute and solvent molecules but does not depend upon their nature and hence, it is a colligative property.

Calculation of molecular mass of solute from relative lowering of vapour pressure. Molecular mass of non-volatile substance can be determined from relative lowering of vapour pressure. A known mass (W_B) of the solute is dissolved in a known mass (W_A) of solvent to prepare a dilute solution and relative lowering of vapour pressure is determined experimentally. Knowing the molecular mass (M_A) of the solvent, molecular mass (M_B) of the solute can be determined as shown under :

$$n_A = \frac{W_A}{M_A}; n_B = \frac{W_B}{M_B}$$

$$X_B = \frac{n_B}{n_A + n_B} = \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

Relative lowering of vapour pressure is given by

$$\frac{\Delta P}{P_A^\circ} = \frac{P_A^\circ - P_A}{P_A^\circ} = X_B$$

$$= \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

For dilute solutions $W_B/M_B << W_A/M_A$ and hence in the above expression W_B/M_B may be neglected in the denominator as compared with W_A/M_A.

$$\therefore \quad \frac{P_A^\circ - P_A}{P_A^\circ} = \frac{W_B/M_B}{W_A/M_A} = \frac{W_B}{M_B} \cdot \frac{M_A}{W_A}$$

or

$$M_B = \frac{W_B \cdot M_A}{W_A} = \left(\frac{P_A^\circ}{P_A^\circ - P_A}\right) \quad ...(3.11)$$

In this equation, all the parameters except M_B are known and hence, M_B can be calculated.

Example 3.18. *The vapour pressure of 2% aqueous solution of an electrolyte XY at 373 K is 755 mm. Calculate the molecular mass of the solute. Vapour pressure of pure water at 373 K is 760 mm.*

Solution. Here,

Mass of the solvent $W_A = 100 - 2 = 98$ g

Mass of the solute $W_B = 2$ g

Molecular mass of solvent $(M_A) = 18$

Molecular mass of solute $(M_B) = ?$

Vapour pressure of pure water $(P_A^\circ) = 760$ mm

Vapour pressure of solution $(P_A) = 755$ mm.

Now,

$$M_B = \frac{W_B M_A}{W_A}\left(\frac{P_A^\circ}{P_A^\circ - P_A}\right)$$

$$= \frac{2 \times 18}{98} \times \frac{760}{760 - 750} = \frac{2 \times 18 \times 760}{98 \times 5} = \mathbf{55.8.}$$

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Example 3.19. *The vapour pressure of pure benzene at 25°C is 639.7 mm of Hg and vapour pressure of a solution of a solute in benzene at same temperature is 631.9 mm of Hg. Calculate the molality of the solution.* (M.L.N.R. 1989)

Solution. Let the molality be m

∴ The solution contains m moles of solute per 1000 g of solvent

Moles of solvent $(n_A) = \frac{1000}{78} = 12.82$

Moles of solute $(n_B) = m$

Vapour pressure of benzene $(P_A°) = 639.7$ mm

Vapour pressure of solution $(P_A) = 631.9$ mm

Now $$\frac{P_A° - P_A}{P_A°} = \frac{n_B}{n_A}$$

or $$\frac{639.7 - 631.9}{639.7} = \frac{m}{12.82}$$

or $$m = \frac{12.82 \times 7.8}{639.7} = \mathbf{0.156\ mol\ kg^{-1}}.$$

Example 3.20. *The vapour pressure of pure benzene at a certain temperature is 640 mm Hg. A non-volatile non-electrolyte solid weighing 2.175 g is added to 39.0 g of benzene. The vapour pressure of the solution is 600 mm Hg. What is the molecular mass of the solid substance ?* (I.I.T. 1990)

Solution.

Mass of solvent (W_A) = 39.0 g

Mass of solute (W_B) = 2.175 g

Vapour pressure of pure solvent $(P_A°)$ = 640 mm

Vapour pressure of solution (P_A) = 600 mm

Molecular mass of solvent (M_A) = 78

Molecular mass of solute (M_B) = ?

$$M_B = \frac{W_B \times M_A}{W_A}\left(\frac{P_A°}{P_A° - P_A}\right)$$

$$= \frac{2.175 \times 78}{39.0}\left(\frac{640}{640 - 600}\right) = \frac{2.175 \times 78}{39.0} \times \frac{640}{40} = 69.6$$

Molecular mass of solute = 69.6.

REVIEW PROBLEMS

3.26. Calculate the vapour pressure of a solution at 100°C containing 3 g cane sugar in 70 g of water. Vapour pressure of pure water at 100°C = 760 mm.

3.27. 5.00 g of a substance with mol. mass 200 have been dissolved in 50 g of a solvent with molecular mass 60 and vapour pressure 400 torr. Find the vapour pressure of the solution.

3.28. A 0.5 M aqueous solution of substance has a density 1 g cm^{-3} at 298 K. Find out its vapour pressure if vapour pressure of pure water at 298 K is 20 torr.

3.29. The vapour pressure of water is 23.75 mm of Hg. Calculate the vapour pressure above 5% aqueous solution of urea. (*CBSE 1986*)

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3.30. A current of dry air was passed through the bulb containing a solution of 6.916 g of organic substance in 100 g of alcohol and then through the bulb containing pure alcohol. The loss in the mass of solution bulb was 0.9675 g and that in the pure alcohol bulb is 0.055 g. Calculate the molecular mass of the organic substance in solution.

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2. Elevation of Boiling Point

As already discussed (Section 3.3) lowering of vapour pressure takes place when a non-volatile solute is added to a volatile solvent. This results in the elevation of boiling point.

The **boiling point** *of a liquid may be defined as the temperature at which its vapour pressure becomes equal to atmospheric pressure.*

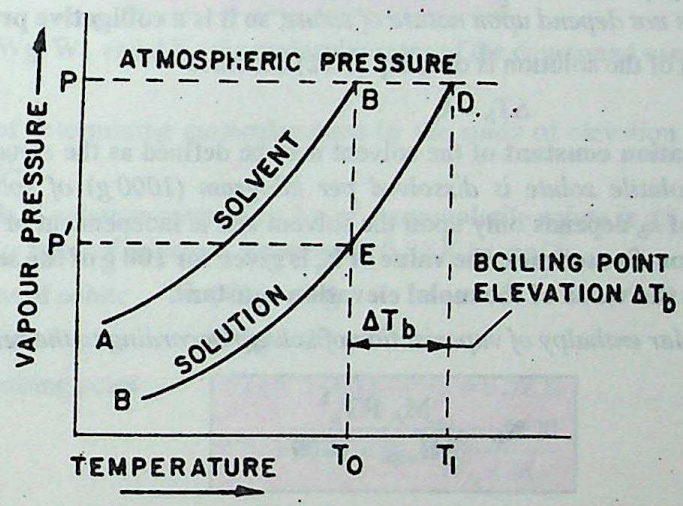

Fig. 3.5. Vapour pressure curves explaining elevation of boiling point.

The effect of addition of a non-volatile solute on the boiling point is shown in Fig. 3.5. The curves AB and CD are the vapour pressure curves for the pure liquid solvent and solution of a non-volatile solute with the solvent respectively. It is evident from the plot that at each temperature the vapour pressure of solution is lower than that of the pure solvent and thus, the vapour pressure curve for the solution runs below that of the pure solvent. At temperature T_0, the vapour pressure of the pure solvent becomes equal to the atmospheric pressure and thus, T_0 is the boiling point of the pure solvent. The vapour pressure of the solution at T_0 is much less than the atmospheric pressure and therefore, it is necessary to heat the solution to a higher temperature, say T_1, in order that its vapour pressure becomes equal to the atmospheric pressure. Thus T_1 is the boiling point of the solution. Thus, it is clear that the solution boils at a higher temperature than the pure solvent. Evidently, $T_1 - T_0$ (or ΔT_b) is the elevation in boiling point. Since its magnitude is determined by the vapour pressure lowering, the elevation in the boiling point is also proportional to the solute concentration. Thus,

$$\Delta T_b \propto \Delta p \propto X_B$$

$$\Delta T_b = kX_B$$

$$= k\frac{n_B}{n_A + n_B} \doteq k\frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

For dilute solutions $\frac{W_B}{M_B} << \frac{W_A}{M_A}$ and hence, $\frac{W_B}{M_B}$ may be neglected in denominator as compared to W_A/M_A.

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$$\therefore \quad \Delta T_b = k\frac{W_B/M_B}{W_A/M_A} = k\frac{n_B}{W_A}M_A \qquad \left[\because \frac{W_B}{M_B} = n_B\right]$$

If W_A is the mass of solvent in kg, then $\frac{n_B}{W_A}$ is equal to molality (m) of the solution

$$\Delta T_b = kM_A\, m$$

Here k and M_A are constants and hence their product, *i.e.*, kM_A is replaced by another constant k_b.

$$\boxed{\Delta T_b = k_b \cdot m} \qquad ...(3.12)$$

where k_b is **molal elevation constant** or **molal ebullioscopic constant.**

As is clear from Eq. (3.12), *elevation in boiling point depends upon the relative number of moles of solute and solvent but does not depend upon nature of solute,* **so it is a colligative property.**

When molality (m) of the solution is one, Eq. (3.12) becomes

$$\Delta T_b = k_b$$

Hence, **molal elevation constant** of the solvent may be defined as the *elevation in its boiling point when one mole of non-volatile solute is dissolved per kilogram (1000 g) of solvent.* The **units of k_b** are **K . kg mol^{-1}.** The value of k_b depends only upon the solvent and is independent of the nature of solute and concentration of the solution. **Sometimes, the value of k_b is given for 100 g of the solvent. In such an event this constant is ten times the value of the molal elevation constant.**

K_b is related to *molar enthalpy of vaporisation of solvent according to the relation.*

$$\boxed{K_b = \frac{M_A RT_b^2}{\Delta H_{vap.} \times 1000}} \qquad ...(3.13)$$

where, M_A = Molecular mass of solvent

R = Universal gas constant

T_b = Boiling point of pure solvent

$\Delta H_{vap.}$ = Enthalpy of vaporisation of solvent.

The molal elevation constants, k_b, for different solvents are given in Table 3.3.

Table 3.3. Data for Molal Elevation Constants

Solvent	*b.p. (K)*	*k_b (K kg mol^{-1})*
Water	373	0.52
Benzene	353.3	2.53
CCl_4	350	5.03
CS_2	319.4	2.34
Chloroform	334.4	3.63
Ethyl alcohol	351.5	1.20
Ether	307.8	2.02
Acetic acid	391.3	3.07
Camphor	481.3	5.95
Nitrobenzene	483.8	5.24

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Calculation of molecular mass of an unknown non-volatile compound from elevation of boiling point. To calculate the molecular mass of an unknown non-volatile compound a known mass (say W_B g) of it is dissolved in a known mass (say W_A g) of some suitable solvent and elevation in its boiling point (ΔT_b) is determined. Let M_B be the molecular mass of the compound. Then

Molality of solution, $$m = \frac{W_B}{M_B}\frac{1000}{W_A}.$$

We know $$\Delta T_b = k_b \times m = k_b \cdot \frac{W_B}{W_A} \cdot \frac{1000}{M_B}$$

$$\boxed{M_B = \frac{k_b \times W_B \times 1000}{W_A \times \Delta T_b}} \quad ...(3.14)$$

Knowing k_b, W_B, W_A and ΔT_b, the molecular mass of the compound can be calculated from the above relation.

The method of determining molecular mass by the study of elevation in boiling point is known as **ebullioscopic method.**

Example 3.21. *A solution containing 2 g of a non-volatile solute in 20 g of water boils at 373.52 K. Find out the molecular mass of solute, k_b for water is 0.52 K kg mol^{-1}.*

Solution. Mass of solute $(W_B) = 2$ g

Mass of solvent $(W_A) = 20$ g

Elevation in boiling point $\Delta T_b = 373.52 - 373 = 0.52$ K

$$\Delta T_b = k_b\, m = k_b \cdot \frac{W_B \times 1000}{W_A \times M_B}$$

or $$M_B = k_b \frac{W_B}{W_A}\frac{1000}{\Delta T_b} = 0.52 \times \frac{2}{20} \times \frac{1000}{0.52} = \mathbf{100.}$$

Example 3.22. *The boiling point of a solution of 0.105 g of a substance in 15.84 g of ether was found to be 0.100°C higher than that of pure ether. What is the molecular mass of the substance.*

Molal elevation constant for ether per 100 g is 21.6. (M.L.N.R. 1991)

Solution. $$M_B = k_b \frac{W_B \times 1000}{\Delta T_b \times W_A}.$$

$k_b = 21.6$ per 100 g or 2.16 per 1000 g

$$\therefore \quad M_B = \frac{2.16 \times 0.105 \times 1000}{0.100 \times 15.84} = \mathbf{143.2.}$$

Example 3.23. *The boiling point of pure water is 373 K. Calculate the boiling point of an aqueous solution containing 19 g of glucose in 100 g of water. Molal elevation constant of water is 0.52 K kg mol^{-1}.*

Solution. Mass of solvent (W_A) = 100 g

Mass of solute (W_B) = 18 g

Molecular mass of solute (M_B) = 180

Molality $$= \frac{W_B \times 1000}{M_B \times W_A} = \frac{18 \times 1000}{180 \times 100} = 1 \text{ mol kg}^{-1}$$

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$$\Delta T_b = k_b \times m$$
$$= 0.52 \times 1 = 0.52 \text{ K}$$

Boiling point of solution $= \begin{bmatrix} \text{Boiling point of} \\ \text{pure solvent} \end{bmatrix} + \begin{bmatrix} \text{Elevation in} \\ \text{boiling point} \end{bmatrix}$

$$= 373 + 0.52 = \mathbf{373.52\ K.}$$

Example 3.24. *A solution prepared by dissolving 1.017 g of naphthalene ($C_{10}H_8$) in 100 g of CCl_4 has a boiling point elevation of 0.4°C. A 1.24 g of an unknown solute in same amount of CCl_4 produced boiling point elevation of 0.62°C. Calculate the molecular mass of unknown solute.*

Solution. *Calculation of K_b for CCl_4*

Here, mass of solvent $(W_A) = 100$ g

Mass of solute $(W_B) = 1.017$ g

Molecular mass of solute, $C_{10}H_8(M_B) = 128$

Elevation in boiling point $(\Delta T_b) = 0.4°$

Now, $$\Delta T_b = k_b \frac{W_B \times 1000}{W_A \times M_B}$$

or $$k_b = \frac{\Delta T_b \times W_A \times M_B}{W_B \times 1000}$$

$$= \frac{0.4 \times 100 \times 128}{1.017 \times 1000} = \mathbf{5.03\ K\ kg\ mol^{-1}}$$

Calculation of molecular mass of unknown solute

Here, mass of solvent $(W_A) = 100$ g

Mass of solute $(W_B) = 1.24$ g

Elevation in boiling point $(\Delta T_b) = 0.62°$

Now, $$M_B = k_b \frac{W_B \times 1000}{W_A \times \Delta T_b} = \frac{5.03 \times 1.24 \times 1000}{100 \times 0.62} = \mathbf{100.6.}$$

REVIEW PROBLEMS

3.31. A solution containing 1.20 g of an organic solute per 50 g of CCl_4 boils at 350.5 K under atmospheric pressure. What is the molecular mass of the solute. Normal boiling point of CCl_4 is 350 K and $k_b = 5.0$ K kg mol^{-1}.

3.32. Calculate the elevation in boiling point when 12.5 g of urea is dissolved in 170 g of water. Molecular mass of urea is 60 and molal elevation constant of water is 0.52 K kg mol^{-1}.

3.33. 10 g of a non-volatile solute when dissolved in 100 g of benzene raises its b.p. by 1°. What is the molecular mass of the solute. k_b for benzene = 2.53 K kg mol^{-1}.

3.34. Find out the boiling point of a solution containing 0.360 g of glucose ($C_6H_{12}O_6$) dissolved in 100 g of water. k_b for water 0.52 K kg mol^{-1}.

3.35. A solution containing 0.730 g of camphor (mol. mass 152) in 36.8 g of acetone (b.p. = 56.30°C) boils at 56.55°C. On the other hand, the solution of 0.564 g of unknown compound in same mass of acetone boils at 56.46°C. Calculate the molecular mass of unknown compound.

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3. Depression in Freezing Point

Freezing point of a substance is the temperature at which solid and liquid phases of the substance coexist. It is defined as the *temperature at which its solid and liquid phases have the same vapour pressure.*

The freezing point of a pure liquid is fixed. Now, if a non-volatile solute is dissolved in the pure liquid to constitute a solution, there occurs a lowering in the freezing point. *Now, for the solution the freezing point shall refer to that temperature at which the vapour pressure of the solvent in two phases, i.e., liquid solution and solid solvent is the same.* Since the solvent vapour pressure in solution is depressed, its vapour pressure will become equal to that of the solid solvent at a lower temperature (Fig. 3.6).

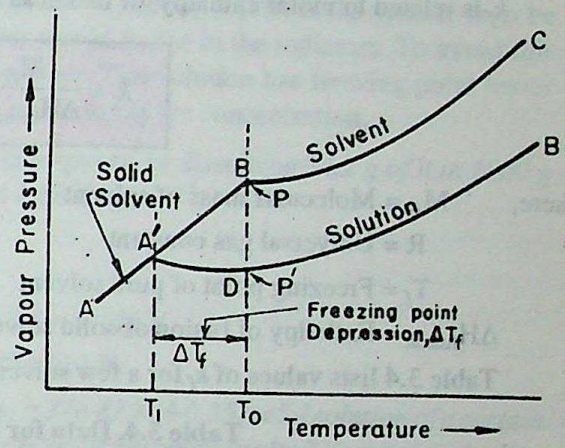

Fig. 3.6. Depression of freezing point.

Here AB, BC and A′B′ are the vapour pressure curves of solid solvent (ice), liquid solvent (water) and solution containing non-volatile solute respectively.

Evidently the freezing point of the pure solvent is the temperature corresponding to the point B (T_0 K) and that of the solution is the temperature corresponding to the point A′ (T_1 K). Clearly, ($T_0 - T_1$) K or ΔT_f is the freezing point depression. Since its magnitude is determined by that of the vapour pressure lowering, *the freezing point depression depends upon the molal concentration of the solute and does not depend upon the nature of solute. It is, therefore, a* **colligative property.** The general relation between these two quantities for a solution of non-electrolyte is usually expressed in term of molality of the solution

$$\Delta T_f \propto \Delta P \propto X_B$$

$$\Delta T_f = kX_B$$

$$= k\frac{n_B}{n_A + n_B} = k\frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

For dilute solution, $\frac{W_B}{M_B} << \frac{W_A}{M_A}$ and hence, $\frac{W_B}{M_B}$ may be neglected in denominator as compared to W_A/M_A.

$$\therefore \quad \Delta T_f = k\frac{W_B/M_B}{W_A/M_A} = k\frac{n_B}{W_A}M_A$$

If W_A is the mass of solvent in kg, then $\frac{n_B}{W_A}$ is equal to molality (m) of the solution

$$\Delta T_f = kM_A m \qquad (\text{As } k \,.\, M_A = k_f)$$

$$\therefore \quad \boxed{\Delta T_f = k_f\, m} \qquad ...(3.15)$$

where k_f is molal depression constant.

As is clear from Eq. (3.15), *depression in freezing point depends upon relative number of moles of solute and solvent but does not depend upon nature of solute, so it is a colligative property.*

When molality (m) of the solution is one, Eq. (3.15) becomes

$$\Delta T_f = k_f$$

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Hence, **molal depression constant** or **molal cryoscopic constant** may be defined as the ***depression in freezing point when one mole of non-volatile solute is dissolved per kilogram (1000 g) of solvent.*** The **units** of k_f are **K kg mol^{-1}**. Also the value of k_f for 100 g of solvent will be ten times the value of molal depression constant.

k_f is related to molar enthalpy of fusion as :

$$k_f = \frac{M_A RT_f^2}{\Delta H_{fusion} \times 1000} \quad ...(3.16)$$

where, M_A = Molecular mass of solvent

R = Universal gas constant

T_f = Freezing point of pure solvent

ΔH_{fusion} = Enthalpy of fusion of solid solvent.

Table 3.4 lists values of k_f for a few solvents.

Table 3.4. Data for Molal Depression Constants

Solvent	*F.P. (K)*	*k_f (K kg mol^{-1})*
Acetic acid	289.6	3.90
Benzene	278.6	5.12
Camphor	452.0	39.7
CS_2	164.2	3.83
CCl_4	250.5	31.8
Chloroform	209.6	4.70
Ether	156.9	1.79
Ethyl alcohol	155.7	1.99
Naphthalene	353.3	6.80
Water	273.0	1.86
Nitrobenzene	278.7	7.00

Calculation of molecular mass of an unknown non-volatile compound from depression in freezing point.

To calculate the molecular mass of an unknown non-volatile compound a known mass (say W_B g) of it is dissolved in a known mass (say W_A g) of some suitable solvent and depression in its freezing point (ΔT_f) is determined. Let M_B be the molecular mass of the compound. Then,

Molality of the solution $$m = \frac{W_B}{M_B}\frac{1000}{W_A}$$

We know $$\Delta T_f = k_f \times m = k_f \cdot \frac{W_B}{W_A} \cdot \frac{1000}{M_B}$$

$$M_B = \frac{k_f \times W_B \times 1000}{W_A \times \Delta T_f} \quad ...(3.17)$$

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Knowing k_f, W_B, W_A and ΔT_f, the molecular mass of the compound can be calculated from the above relation.

The method of determining molecular mass by the study of depression in freezing point is called **cryoscopic method.**

Antifreeze solutions. Water is used in radiators of vehicles as cooling liquid. If the vehicle is to be used at high altitudes where the temperature is sub-zero, water would freeze in the radiators. To avoid this difficulty, a solution of ethylene glycol in water is used in radiators. This solution has freezing point lower than zero. Freezing point can be lowered to the desired extent by changing the concentration.

Example 3.25. *Solution of sucrose (mol. mass = 342) is prepared by dissolving 34.2 g of it in 1000 g of water. Find out freezing point of the solution. k_f for water is 1.86 K kg mol^{-1}.*

Solution. Molality of the solution $= \frac{34.2}{342} = 0.1$

$$\Delta T_f = k_f \times m = 1.86 \times 0.1 = 0.186 \text{ K}$$

Freezing point of solution $= 273 - 0.186 =$ **272.814 K.**

Example 3.26. *The normal freezing point of nitrobenzene is 278.82 K. A 0.25 molal solution of a certain non-volatile solute in nitrobenzene causes a lowering of freezing point of nitrobenzene by 2 degrees. Calculate the molal depression constant (k_f).*

Solution. Molality $(m) = 0.25\ m$

$$\Delta T_f = 2 \text{ K}$$

$$\Delta T_f = k_f \times m$$

$$k_f = \frac{\Delta T_f}{m} = \frac{2 \text{ K}}{0.25 \text{ mol kg}^{-1}} = \mathbf{8\ K\ kg\ mol^{-1}}.$$

Example 3.27. *An aqueous solution of a weak monobasic acid containing 0.1 g in 21.7 g of water freezes at 272.817. If the value of k_f for water is 1.86 K kg mol^{-1}, what is the molecular mass of the acid ?*

Solution. Mass of solvent $(W_A) = 21.7$ g

Mass of solute $(W_B) = 0.1$ g.

Depression in freezing point $(\Delta T_f) = 273 - 272.817 = 0.183$ K

$$\Delta T_f = k_f \times m = k_f \cdot \frac{W_B}{W_A} \times \frac{1000}{M_B}$$

$$M_B = \frac{k_f \times W_B \times 1000}{W_A \times \Delta T_f} = \frac{1.86 \times 0.1 \times 1000}{21.7 \times 0.183} = \mathbf{46.8}.$$

REVIEW PROBLEMS

3.36. Find out the freezing point of solution containing 3.6 g of glucose (mol. mass = 180) dissolved in 50 g of water. k_f for water = 1.86 K kg mol^{-1}.

3.37. A solution containing 2.0 g of a non-volatile solute in 120.0 g of water has a freezing point 272.91 K. If the value of k_f for water is 1.86 K kg mol^{-1}, what is the molecular mass of the solute ?

3.38. A solution containing 18 g of non-volatile solute in 200 g of water freezes at 272.07 K. Calculate the molar mass of the solute. ***(CBSE 1993)***

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3.39. An aqueous solution of a weak monobasic acid containing 0.1 g in 21.7 g of water freezes at 272.81 K. If the value of K_f for water is 1.86 K kg mol^{-1}, what is the molecular mass of the monobasic acid ?

3.40. A solution containing 25.6 g of sulphur dissolved in 1000 g of naphthalene gave a freezing point lowering of 0.680. Calculate the molecular formula of sulphur, k_f for naphthalene = 6.8 K kg mol^{-1}.

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4. Osmotic Pressure

When a solution is separated from pure solvent by a semi-permeable membrance* then it is observed that the solvent flows from the region of pure solvent into solution. Similarly, if two solutions of different concentrations are separated by a semi- permeable membrane then the solvent flows from solution of lower concentration into solution of higher concentration. **The passage of solvent from pure solvent or from solution of lower concentration into solution of higher concentration through a semi-permeable membrane is called osmosis.**

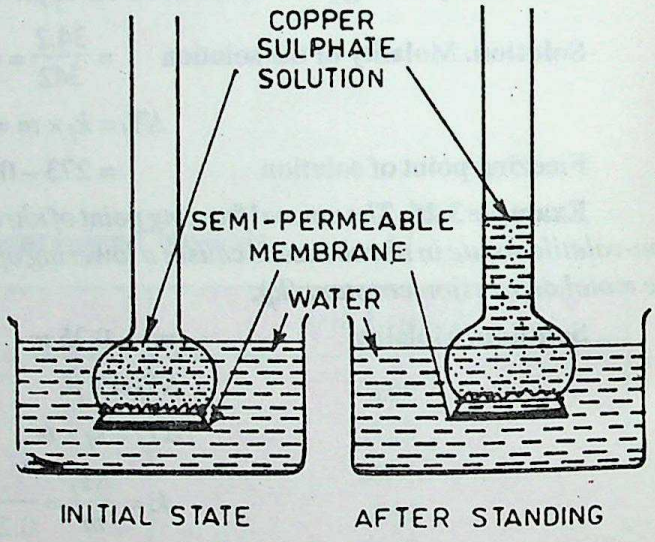

Fig. 3.7. Osmosis.

In order to understand osmosis, take a thistle funnel covered with semi-permeable membrane and put $CuSO_4$ solution in it. Now place this funnel in a beaker containing pure water. It is observed that water flows from beaker into the funnel (Fig. 3.7). As a result of this the level of solution in funnel starts rising. After some time the level of solution in the thistle funnel becomes constant indicating that process of osmosis has stopped. At this stage hydrostatic pressure of the column is sufficient to stop inward flow of solvent into solution. *The excess hydrostatic pressure which builds up as a result of osmosis is called osmotic pressure.*

Thus, the **osmotic pressure** of the solution at a particular temperature may be defined as the ***excess hydrostatic pressure that builds up when the solution is separated from the solvent by a semi-permeable membrane.*** It is denoted by π.

A very curious question may strike at this juncture as to why do such a phenomenon takes place ? The answer to the problem can be developed in terms of difference in vapour pressure of the solvent and solution (or between the two solutions). Now in a solution, the escaping tendency of the solvent is less as compared to that in a pure solvent, therefore, the vapour pressure of solution is less than that of pure solvent. This difference in vapour pressure permits the transfer of solvent molecules from pure solvent into solution.

The osmotic pressure can be defined in another way. In order to understand this, let us consider the phenomenon of osmosis in a special type of apparatus as shown in Fig. 3.8.

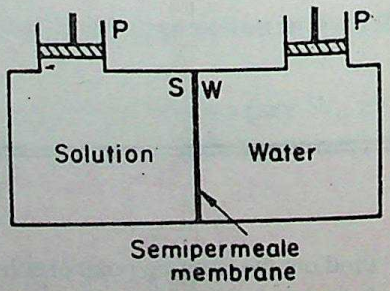

Fig. 3.8. Definition of osmotic pressure (*diagrammatic*).

***A semi-permeable membrane** *is a membrane which allows solvent molecules to pass through it but does not allow the solute particles to pass through it.* Animal bladder is an example of natural semi-permeable membrane. Parchment paper, cellophane and copper ferrocyanide are some examples of artificial semi-permeable membranes.

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The apparatus consists of a chamber divided into two water-tight compartments (S and W) by a semi-permeable membrane and fitted with the water-tight pistons. On putting the solution in compartment S and water in the compartment W, the piston P will be displaced upwards due to the movement of water from W to S. To stop this movement of water, we have to apply mechanical pressure on solution side. The pressure just sufficient to stop osmosis will be the osmotic pressure.

Thus, the **osmotic pressure** may also be defined as the ***excess pressure that must be applied to the solution side to prevent the passage of solvent into it through a semi-permeable membrane.***

Reverse Osmosis

If the pressure applied on the solution is greater than the osmotic pressure then solvent starts passing from solution into solvent. This is called **reverse osmosis.** The phenomenon of reverse osmosis is generally used for purification of sea water or hard water. Sea water, (which is dilute solution of many undesirable salts is placed in contact with pure water through semi-permeable membrane. Pressure greater than osmotic pressure is applied on sea water. This causes the movement of pure water from sea water side to pure water side.

Isotonic, Hypertonic and Hypotonic Solutions

The two solutions having equal osmotic pressure are called **isotonic solutions.** A solution having higher osmotic pressure than some other solution is said to be **hypertonic** with respect to the other solution. A solution having lower osmotic pressure relative to some other solution is called **hypotonic.**

Normal saline solution (0.9% NaCl solution) is isotonic with respect to human blood. Therefore, during intravenous injections, the medicines are mixed with saline water before the injection. This prevents the blood cells from shrinking or brusting. For example, if the solution is less concentrated, its osmotic pressure will be low, and water will move into the cell causing it to swell and finally brust. On the other hand, if the solution is more concentrated its osmotic pressure is high and the water will move out of the cell causing the cell to shrink.

The osmotic pressure is a colligative property. For a given solvent the osmotic pressure depends only upon the molar concentration of solute but does not depend upon its nature. Osmotic pressure is related to the number of moles of the solute by the following relation :

$$\pi V = nRT \qquad ...(3.18)$$

or

$$\pi = \frac{n}{V} RT$$

$$\pi = CRT \qquad ...(3.19)$$

Here, C = concentration of solution in moles per litre
R = gas constant
T = Temperature
n = number of moles of solute
V = volume of solution.

Eq. (3.18) is called **Van't Hoff's solution equation.**

Osmotic pressure is related to relative *lowering of vapour pressure, elevation of boiling point* and *depression freezing point* according to the following relations.

(*i*)
$$\pi = \left(\frac{P_A^\circ - P_A}{P_A^\circ}\right) \times \frac{dRT}{M_B} \qquad ...(3.20)$$

(*ii*)
$$\pi = \Delta T_b \times \frac{dRT}{1000 \times K_b} \qquad ...(3.21)$$

(*iii*)
$$\pi = \Delta T_f \times \frac{dRT}{1000 \times K_f} \qquad ...(3.22)$$

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In the above relations, π = Osmotic pressure

d = Density of solution at temperature T

R = Universal gas constant

M_B = Mol. mass of solute

K_b = Molal elevation constant of solvent

K_f = Molal depression constant of solvent.

Table 3.5. Difference between Osmosis and Diffusion

	Osmosis	*Diffusion*
1.	In osmosis the movement of molecules takes place through a semi-permeable membrane.	In diffusion there is no role of semi-permeable membrane.
2.	It involves movement of only solvent molecules from one side to the other.	It involves passage of solvent as well as solute molecules from one region to the other.
3.	Osmosis is limited to solutions only.	Diffusion can take place in liquids, gases and solutions.
4.	Osmosis can be stopped or reversed by applying additional pressure on the solution side.	Diffusion can neither be stopped nor reversed.

Determination of Osmotic Pressure

Berkley and Hartley's Method. This method involves the measurement of external pressure which is just sufficient to prevent the entry of solvent into solution through a semi-permeable membrane. This pressure is equal to the osmotic pressure of the solution.

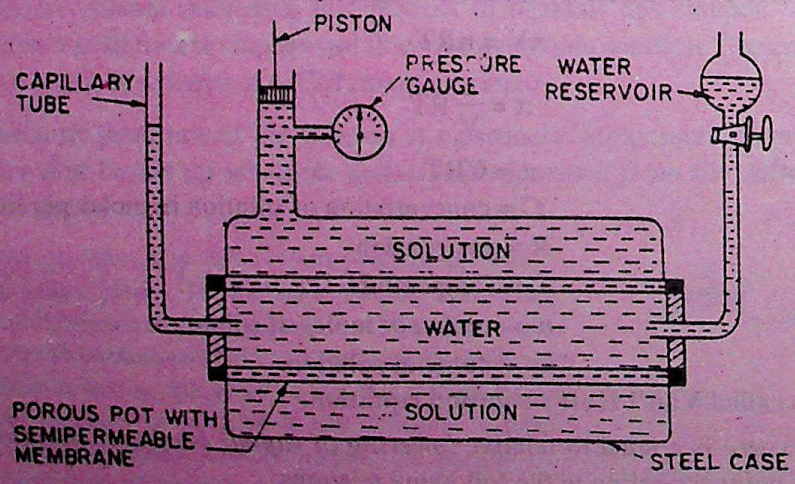

Fig. 3.9. Determination of Osmotic Pressure.

The apparatus consists of a strong vessel made up of steel into which a porous pot is fitted. The walls of the porous pot are coated with a semi-permeable membrane of copper ferrocyanide. The porous pot is fitted with a capillary tube on one side and water reservoir on the other. The steel vessel is fitted with a piston and pressure gauge as shown in Fig. 3.9.

Water and solution are taken in the porous pot and steel vessel respectively. Due to osmosis, water tends to move into steel vessel from the porous pot through the membrane. It is indicated by the fall in water level in the capillary tube. This flow of water is stopped by applying the pressure on the solution with the help of the piston, so that the level of water in the capillary tube does not change. The pressure so applied is equal to the osmotic pressure and can be measured from the pressure gauge.

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Determination of Molecular Mass from Osmotic Pressure

In order to determine the molecular mass of an unknown non-volatile compound, a known mass (say W_B g) of the compound is dissolved to prepare a known volume (say V litres) of solution and the osmotic pressure of the solution is determined. From this, the molecular mass of the compound is calculated as discussed under :

According to Van't Hoff equation, $\pi = \frac{n_B}{V} RT$

where n_B is the number of moles of the solute and is given by $\frac{W_B}{M_B}$.

Here, W_B is the mass of the solute and M_B is the molecular mass of the solute.

$$\therefore \quad \pi = \frac{W_B RT}{VM_B}$$

or

$$M_B = \frac{W_B RT}{\pi V} \quad ...(3.23)$$

By applying the formula given in Eq. (3.23), molecular mass of the solute can be calculated.

This method is especially suitable for the determination of molecular masses of ***macromolecules*** *such as proteins and polymers. This is due to the reason that for these substances the values of other colligative properties such as elevation in boiling point or depression in freezing point are too small to be measured. On the other hand, osmotic pressure of such substances are measurable.*

Conditions for getting accurate value of molecular mass :

(*i*) *The solute must be non-volatile.*

(*ii*) *The solution must be dilute.*

(*iii*) *The solute should not undergo dissociation or association in the solution.*

Example 3.28. *Calculate the osmotic pressure of a solution containing 3.42 g of sucrose per litre at 400 K. Molecular mass of sucrose is 342. R = 0.082 lit atm mol^{-1} K^{-1}.*

Solution. We know that $\pi = \frac{n_B}{B} RT$

No. of moles of solute (n_B) $= \frac{3.42}{342} = 0.01$ mole

Volume of solution (V) = 1 litre

T = 400 K

$$\pi = \frac{n_B RT}{V} = \frac{0.01 \times 0.082 \times 400}{1} = \mathbf{0.328\ atm.}$$

Example 3.29. *At 298 K, 100 cm^3 of a solution containing 3.002 g of an unidentified solute exhibits an osmotic pressure of 2.55 atm. What is the molecular mass of the solute ?*

Solution. V = 100 cm^3 = 0.1 litre

T = 298 K

W_B = 3.002 g

π = 2.55 atm.

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$$\pi = \frac{n_B RT}{V}; \quad n_B = \frac{\pi V}{RT}$$

$$n_B = \frac{2.55 \times 0.1}{0.082 \times 298} = 0.0104 \text{ moles}$$

$$nB = \frac{W_B}{M_B}$$

$$M_B = \frac{W_B}{n_B} = \frac{3.002}{.0104} = \mathbf{288.6.}$$

REVIEW PROBLEMS

3.41. An aqueous solution of glucose $C_6H_{12}O_6$ has an osmotic pressure of 2.72 atm at 298 K. How many moles of glucose were dissolved per litre of solution.

3.42. Calculate the osmotic pressure of a solution containing 1 g of glucose per 100 mL of the solution at 25°C. Molecular mass of glucose = 180. (R = 8.3141 J mol^{-1}).

3.43. Osmotic pressure of a solution containing 20 g of a polymer per 100 cm^3 of the solution at 298 K is 60 cm Hg. Calculate the molecular mass of the polymer, R = 0.83 litre atm. mol^{-1} deg^{-1}.

3.44. A solution of glucose (molecular mass = 180) is prepared by dissolving 36 g in 1000 g of water. What is

(*i*) the vapour pressure of the solution at 293 K

(*ii*) the osmotic pressure at 298 K

(*iii*) the boiling point of solution

(*iv*) the freezing point of solution.

The vapour pressure of water at 293 K is 17.5 mm of Hg.

3.45. Osmotic pressure of a solution containing 7 g of a protein per 100 ml of solution is 25 mm Hg at 37°C. Calculate the molecular mass of the protein. [*A.I. CBSE (O) 1987, 93*]

3.46. 10 g of a non-volatile solute dissolved in one litre shows an osmotic pressure of 2×10^{-3} atm at 300 K. Calculate the molecular mass of the solute.

3.47. Calculate the osmotic pressure of a solution containing 0.1 mole of a non-electrolyte solute per litre at 273 K. (R = 0.082 litre atm. mol^{-1} K^{-1}). [*Har. (Sc.) 1989*]

3.48. A 5% solution of cane sugar (molar mass = 342) is isotonic with 0.877% solution of urea. Find the molecular mass of urea. [*Har (Sc.) 1988 ; Pb. 1993*]

3.49. Osmotic pressure of a solution containing 2 g of dissolved protein per 300 cm^3 of solution is 20 mm of Hg at 27°C. Calculate the molecular mass of protein. (R = .0821 L atm. mol^{-1} K^{-1}). [*CBSE (1) 1992*]

3.50. The osmotic pressure of blood at 37°C is 8.21 atm. How much glucose should be used per litre for an intravenous injection so that it is isotonic with blood.

Biological Importance of Osmosis

Osmosis plays an important role in absorption of water by the plants from the soil. Plants and animal bodies are made of very large number of cells. Each cell is made of living cytoplasmic walls which act as semi-permeable membranes. A cell also contains a fluid called **cell sap.** The osmotic pressure of cell sap is generally very high. Therefore, when the plant cells (in the roots) come in contact with soil water, it moves into the cell sap due to osmosis. The water, thus, absorbed is further transported to the stem and other parts of the plant.

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3.8. ABNORMAL MOLECULAR MASSES

It has been widely illustrated in the previous sections as to how molecular masses can be calculated by measuring any of the colligative properties. The relation between *colligative property* and *molecular mass* of the solute is based on the following assumptions :

(*i*) *The solution is dilute, so that Raoult's Law is obeyed.*

(*ii*) *The solute neither undergoes dissociation nor association in solution.*

When we measure the colligative properties of the solutions where above assumptions are not valid we find discrepencies between the observed and calculated values of colligative properties.

These anomalies are primarily due to :

(*i*) *Association of solute molecules* and

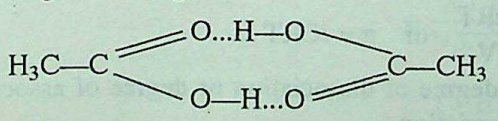
(*ii*) *Dissociation of the solute particles.*

(*i*) **Association of solute molecules**

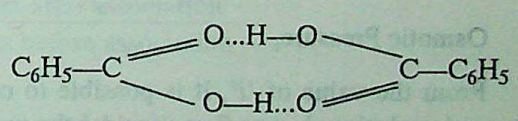
Certain solutes in solution are found to associate. This eventually leads to a decrease in the number of molecular particles in the solutions. Thus, it result in a decrease in the values of colligative properties. As already discussed, the colligate properties are inversely related to the molecular mass,

$$\textit{colligative property} \propto \frac{1}{\textit{molecular mass of solute}}$$, therefore, higher values are obtained for molecular masses than normal values for unassociated molecules.

For example, acetic acid dissolved in benzene shows a molecular mass of 120 (normal molecular mass is 60). Similarly, benzoic acid dissolved in benzene is found to have molecular mass double of its normal molecular mass. This is explained by the fact, that both acetic acid and benzoic acid form *dimers* in solution due to hydrogen bonding.



Acetic acid



Benzoic acid

(*ii*) **Dissociation of solute molecules**

A number of electrolytes dissociate in solution to give two or more particles (ions). Therefore, the number of solute particles, in solutions of such substances, is more than the expected value. Accordingly, such solutions exhibit higher values of colligative properties. Since colligative properties are inversely proportional to molecular masses, therefore, molecular masses of such substances as calculated from colligative properties will be less than their normal values.

For example, KCl dissociates into K^+ and Cl^- ions when dissolved in water. So the number of solute particles in its solution would be double the number of particles if no dissociation had taken place. Hence, it is expected to have molecular mass (on the basis of colligative properties) equal to half of its normal molecular mass, *i.e.*, $\frac{74.5}{2}$ or 37.25. However, the molecular mass of KCl is found to be 40.3 by studies of depression in freezing point. The difference in the two values is due to the fact that there are strong attractive forces present in the oppositely charged ions of the strong electrolyte in solution. These electrical forces hold together a number of the ion pairs. Thus, such electrolytes are incompletely dissociated and the number of the ions formed in solution is not exactly the double but is somewhat less. Consequently, there is difference in the values of molecular masses.

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Van't Hoff's Factor

In 1886, Van't Hoff introduced a factor 'i' called Van't Hoff's factor, to express the extent of association or dissociation of solutes in solution. It is ratio of the normal and observed molecular masses of the solute, *i.e.*,

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}}.$$

In case of association, observed molecular mass being more than the normal, the factor i has value less than 1. But in case of dissociation, the Van't Hoff's factor is more than 1 because the observed molecular mass has a lesser value than the normal molecular mass. In case there is no dissociation the value of 'i' becomes equal to one.

No. Association or dissociation (i = 1)	Association (i < 1)	Dissociation (i > 1)

Since colligative properties are inversely proportional to molecular masses, the Van't Hoff's factor may also be written as :

$$i = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative property assuming no association or dissociation}}$$

$$i = \frac{\text{No. of particles after association or dissociation}}{\text{No. of particles before association or dissociation}}$$

Introduction of the Van't Hoff factor modifies the equations for the colligative, properties as follows :

Relative lowering of vapour pressure, $\frac{P_A^\circ - P_A}{P_A^\circ} = i\,X_B$

Elevation of Boiling Point, $\Delta T_b = ik_b\,m$

Depression of Freezing Point, $\Delta T_f = ik_f\,m$

Osmotic Pressure, $\pi = \frac{inRT}{V}$ or $\pi = iCRT$

From the value of 'i', it is possible to calculate degree of dissociation or degree of association of substance in solution. Let us first consider the case of dissociation.

Degree of Dissociation. *It is defined as the fraction of total molecules which dissociate into simpler molecules or ions.*

In order to calculate the degree of dissociation let us suppose that each molecule of a substance on dissociation gives m particles and that α is the degree of dissociation. Then *for each mole of the substance dissolved.*

Number of moles dissociated $= \alpha$

Number of moles left undissociated $= 1 - \alpha$

Total number of particles at equilibrium $= (1 - \alpha) + m\alpha$

$$\text{Van't Hoff's factor} = \frac{\text{Observed value of colligative property}}{\text{Calculated value of colligative property assuming no dissociation}}$$

or

$$i = \frac{\text{No. of particles after dissociation}}{\text{No. of particles before dissociation}}$$

$$i = \frac{(1 - \alpha) + m\alpha}{1} = 1 + (m - 1)\,\alpha$$

$$\boxed{\alpha = \frac{i - 1}{m - 1}}$$

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For the electrolytes of the type AB, such as NaCl, KCl etc., the number of particles in solution *i.e.*, $m = 2$.

$$\therefore \quad \alpha = i - 1.$$

Similarly, for the electrolytes of the type AB_2, like $CaCl_2$, the value of $m = 3$ and hence,

$$\alpha = \frac{i-1}{2}.$$

Degree of Association. *It is defined as the fraction of the total number of molecules which associate or combine together resulting in the formation of a bigger molecules.*

In order to calculate the degree of association let us suppose that if m particles of the solute associate to form one particle and α is the degree of association as given in the following equation

No. of moles in the beginning $\quad mA \rightleftharpoons [A]_m$

$\quad\quad 1 \quad\quad\quad 0$

Number of moles after association $= (1-\alpha)\dfrac{\alpha}{m}$.

The number of associated moles $= \dfrac{\alpha}{m}$

The number of unassociated moles $= 1 - \alpha$

Total number of particles at equilibrium $= \left(1 - \alpha + \dfrac{\alpha}{m}\right)$ moles

Thus, the Van't Hoff factor, i,

$$i = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

$$= \frac{\text{No. of particles after association}}{\text{No. of particles before association}}$$

$$= \frac{1 - \alpha + \dfrac{\alpha}{m}}{1} = 1 + \alpha\left(\frac{1}{m} - 1\right)$$

or $$\alpha\left(\frac{1}{m} - 1\right) = i - 1$$

Hence, $$\boxed{\alpha = \frac{i-1}{1/m - 1}}.$$

Example 3.30. *0.1 mole of sugar was dissolved in one kg of water. Depression in freezing point was found to be 0.186 K. What conclusion would you draw about the molecular state of sugar ? k_f for water 1.86 K kg mol^{-1}.*

Solution. Molality of solution $= 0.1$

$$k_f = 1.86 \text{ K kg mol}^{-1}$$

Experimentally observed depression in freezing point,

$$\Delta T_{f(exp)} = 0.186 \text{ K}$$

Calculated depression in freezing point

$$\Delta T_{f(cal)} = k_f \times m = 1.86 \times 0.1 = 0.816 \text{ K}$$

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$$i = \frac{\Delta T_{f(exp)}}{\Delta T_{f(cal)}} = \frac{0.186}{0.186} = 1.$$

Since 'i' is equal to one so sucrose molecules are neither associated nor dissociated.

Example 3.31. *Calculate the amount of KCl which must be added to 1 kg of water so that the freezing point is depressed by 2 K. Assume that KCl undergoes complete dissociation*

k_f for water = 1.86 K kg mol^{-1}.

Solution. $KCl \longrightarrow K^+ + Cl^-$

Since one mole of KCl gives 2 mole particles, the value of

$$i = 2$$

$$\Delta T_f = 2 \text{ K}$$

$$k_f = 1.86 \text{ kg mol}^{-1}$$

Applying equation, $\Delta T_f = ik_f m$

$$m = \frac{\Delta T_f}{ik_f} = \frac{2}{2 \times 1.86} = \mathbf{0.54 \text{ mole per kg.}}$$

Therefore, 0.54 mole of KCl should be added to one kg of water.

Molar mass of KCl $= 39 + 35.5 = 74.5$ g

Amount of KCl $= 0.54 \times 74.5 = \mathbf{40.23}$ g

Thus, 40.23 g of KCl should be added to one kg of water.

SOME MISCELLANEOUS EXAMPLES

Example 3.32. *A substance X (mol. moss = 94) associates as $2X \rightleftharpoons X_2$ when dissolved in CCl_4. If 10 g of X is dissolved in 2 kg of CCl_4, the freezing point is lowered by 1.08°C, K_f for CCl_4 is 31.8 K kg mol^{-1} calculate the degree of association of X.*

Solution. *Calculation of observed molecular mass*

$$M_B = \frac{K_f \times W_B \times 1000}{\Delta T_f \times W_A} = \frac{31.8 \times 10 \times 1000}{1.08 \times 2000} = \mathbf{147.2}$$

Calculation of Van't Hoff factor i

$$i = \frac{\text{Normal molecular mass}}{\text{Observed molecular mass}} = \frac{94}{147.2} = \mathbf{0.638}$$

Calculation of degree of association (α)

$$\alpha = \frac{i - 1}{1/m - 1}$$

Since X undergoes dimerisation $\therefore \quad m = 2$

$$\therefore \quad \alpha = \frac{0.638 - 1}{1/2 - 1} = \frac{0.638 - 1}{0.5 - 1} = \frac{-0.362}{-0.5}$$

$$= 0.724 \text{ or } \mathbf{72.4\%}.$$

Example 3.33. *A decimolar solution of potassium ferrocyanide at 300 K is 50% dissociated. Calculate the osmotic pressure of the solution.*

(Roorkee Ent. 1991)

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Solution. $K_4[Fe(CN)_6] \rightleftharpoons 4K^+ + [Fe(CN)_6]^{4-}$

Since one molecule dissociates into five particles

$\therefore$ $m = 5$

Degree of dissociation $\alpha = 50\%$ or 0.5

Now degree of dissociation α is given by

$$\alpha = \frac{i-1}{m-1}$$

or $$0.5 = \frac{i-1}{5-1}$$

or $$i - 1 = 4 \times 0.50 = 2$$

$$i = 2 + 1 = \mathbf{3}$$

Calculation of osmotic pressure

$$\pi = iCRT$$

Here, $C = \frac{1}{10}$ mol L^{-1}

$R = 0.082$ L-atm K^{-1} mol^{-1}

$T = 300$ K

$\therefore$ $\pi = 3 \times \frac{1}{10} \times 0.082 \times 300 =$ **7.38 atm.**

Example 3.34. *The degree of dissociation of $Ca(NO_3)_2$ in dilute aqueous solution contain 7.0 g of the salt per 100 g of water at 100°C is 70%. If vapour pressure of water at 100°C is 760 mm, calculate the vapour pressure of the solution.* (I.I.T. J.E.E. 1992)

Solution. Calcium nitrate dissociates as

$$Ca(NO_3)_2 \longrightarrow Ca^{2+} + 2NO_3^-$$

Since one molecule dissociates into three particles

$\therefore$ $m = 3$

Degree of dissociation $(\alpha) = 0.7$

Now $$\alpha = \frac{i-1}{m-1}$$

or $$0.7 = \frac{i-1}{3-1}$$

or $$i - 1 = 2 \times 0.7 = 1.4$$

$$i = 1.4 + 1 = 2.4$$

Now relative lowering of vapour pressure is given as

$$\frac{P_A^\circ - P_A}{P_A^\circ} = i \cdot \frac{W_B/M_B}{W_A/M_A}$$

Here, $P^\circ = 760$ mm

$W_B = 7$ g

$W_A = 100$ g

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$$M_B = 40 + 2\,(14 + 48) = 164$$

$$M_A = 18$$

$$\therefore \quad \frac{760 - P_A}{760} = \frac{2.4 \times 7 \times 18}{100 \times 164}$$

or

$$760 - P_A = \frac{2.4 \times 7 \times 18 \times 760}{100 \times 164} = 14.01$$

$$\therefore \quad P_A = 760 - 14.01 = 745.99 \text{ mm}$$

$$\approx \mathbf{746\ mm.}$$

Example 3.35. *Calculate the number of molecules of oxalic acid ($H_2C_2O_4 \cdot 2H_2O$) in 100 ml of 0.2 N oxalic acid solution.* (Roorkee Entrance 1991)

Solution. Here, normality $= 0.2$ N

Volume of solution $= 100$ mL

No. of gm equivalents of oxalic acid $= 0.2 \times 100 \times 10^{-3}$

Mass of oxalic acid $= 0.2 \times 100 \times 10^{-3} \times$ Eq. mass

$= 0.2 \times 100 \times 10^{-3} \times 63$ g $= 1.26$ g

Mol. mass of oxalic acid $= 126$

126 g of oxalic acid contains molecules $= 6.02 \times 10^{23}$

1.26 g of oxalic acid contains molecules $= \dfrac{6.02 \times 10^{23}}{126} \times 1.26 = \mathbf{6.02 \times 10^{21}}$.

REVIEW PROBLEMS

3.51. Calculate the amount of NaCl which must be added to 100 g water so that the freezing point is depressed by 2 K. For water $k_f = 1.86$ K kg mol^{-1}. *(A.I. CBSE 1992)*

3.52. Solution of KCl containing 7.45 g of it per litre has osmotic pressure 4.68 atm at 300 K. Calculate its Van't Hoff's factor and degree of dissociation.

3.53. 1.2% solution of NaCl is isotonic with 7.2% solution of glucose (Mol. mass = 180). Calculate the degree of dissociation and Van't Hoff's factor for NaCl solution.

3.54. A sample of water was found to contain dissolved oxygen (O_2) to the extent of 4 ppm and hardness due to Ca^{2+} ions as 3 ppm. Calculate the amount of O_2 and number of Ca^{2+} ions in 1 litre of water (Assume density 1 g/ml).

3.55. Calculate osmotic pressure of the solution obtained by mixing 100 mol of 1.5% (mass-volume) of urea and 100 ml of 3.42% (mass-volume) solution of cane sugar at 20°C. (R = 0.0821 L-atm K^{-1} mol^{-1}).

3.56. Antifreeze/coolant used in car radiators is a solution of ethylene glycol, $(CH_2OH)_2$. In order to prevent the solution from freezing at – 0.3°C, how much ethylene glycol be added to 5 kg of water. ($K_f = 1.86$ K kg mol^{-1}).

3.57. Calculate molality of 99% (by mass) solution of sulphuric acid having density 1.9 g/ml. *(A.I. CBSE 1993)*

3.58. Addition of 0.643 g of a compound to 50 ml benzene ($d = 0.879$ g/mL) lowers its freezing point from 5.51°C to 5.03°C. Calculate molecular mass of the compound. (K_f for benzene = 5.12 K kg mol^{-1}). *(I.I.T., J.E.E. 1992)*

3.59. Average osmotic pressure of human blood is 7.4 atm at 27°C. Calculate total concentration of various solutes. Assuming this concentration to be molality, calculate the freezing point of blood. ($K_f = 1.86$ K kg molal^{-1}).

3.60. A solution containing 2.47 g of ethyl benzoate in 100 g of benzene had density 0.8 g/ml and vapour pressure 742.6 mm of Hg at 80°C. The vapour pressure of pure benzene at same temperature is 751.6 mm of Hg. What is the osmotic pressure of the solution ?

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3.61. Calculate the osmotic pressure of the solution obtained by mixing 100 ml of 1.5% solution of urea (mol. mass 60) and 100 ml of 3.42% solution of cane sugar (mol. mass 432) at 20°C.
($R = 0.082$ L atm K^{-1} mol^{-1})
Find out osmotic pressure due to urea ($\pi_1 = 3$ atm) and that due to sugar ($\pi_2 = 1.2$ atm). Add the two to get total osmotic pressure.

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IMPORTANT TERMS CONCEPTS AND FORMULAE

- **Solution.** A homogeneous mixture of two or more substances whose concentration can be varied with in certain limits.
- **Saturated solution.** A solution which cannot dissolve any more of the solute at a particular temperature.
- **Solubility.** The amount of the solute present in 100 g of the solvent in a saturated solution at particular temperature.
- **Super saturated solution.** A solution in which the amount of solute present in 100 g of the solvent at a particular temperature is more than its normal solubility at that temperature.
- **Mass per cent.** Mass of solute per 100 g of solution.
- **Molarity.** Number of moles of solute per litre of solution.
- **Normality :** Number of gram-equivalents of solute per litre of solution.
- **Molality.** Number of moles of solute per kilogram of solvent.
- **Mole fraction.** Ratio of number of moles of a component to total number moles.
- **Parts per million.** The number of parts by mass of solute per million parts by mass of solution.
- **Vapour Pressure.** The pressure developed above the liquid at particular temperature at the equilibrium point.
- **Raoult's Law.** The vapour pressure of a solution is equal to the product of mole fraction of the solvent and its vapour pressure in pure state.
- **Lowering of Vapour Pressure :** It is the difference in the vapour pressure of the pure solvent and that of solution.
- **Ideal Solution.** The solution which obey Raoult's law at all concentrations and follow the conditions $\Delta H_{mix} = 0$; $\Delta V_{mix} = 0$.
- **Non-Ideal Solution.** The solution which show positive or negative deviations from Raoult's law.
- **Azeotrope.** The mixture of liquids which boils at constant temperature like pure liquid and has same composition of component in liquid as well as vapour phase.
- **Colligative Properties.** The properties of the solution which are independent of nature of solute but depend upon the concentration if solute particles.
- **Relative lowering of vapour pressure.** The ratio of the lowering of vapour pressure to be vapour pressure of pure solvent.
- **Molal elevation constant.** The elevation in the boiling point of the solution when its molality is unity. It is also called molal ebullioscopic constant.
- **Molal depression constant.** The depression in the freezing point when the molality of the solution is unity. It is also called molal cryosocopic constant.
- **Osmosis.** The passage of solvent from pure solvent or solution of low concentration to the solution of higher concentration through the semi-permeable membrane.
- **Osmotic Pressure.** The excess pressure that must be applied to the solution side to prevent the passage of solvent into it through semi-permeable membrane.

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- **Isotonic solutions.** The solutions of same molar concentration and same osmotic pressure at particular temperature.
- **Isopiestic solutions.** The solutions whose vapour pressure are equal at particular temperature.
- **Van't Hoff factor.** It is the ratio of normal molecular mass to observed molecular mass or the ratio of observed colligative property to normal colligative property.

IMPORTANT FORMULAE

In the formulae given below ; subscript A is used for solvent and B is used for solute : Also.

W_A = Mass of solvent in gram ; W_B = Mass of solute in grams

M_A = Mol. mass of solvent ; M_B = Mol. mass of solute

V = Volume of solution ; V_A = Volume of solvent ;

V_B = Volume of solute

Mass % $= \dfrac{W_B}{W_A + W_B} \times 100$ **Volume %** $= \dfrac{V_B}{V_A + V_B} \times 100$

Molarity $(M) = \dfrac{n_B}{V_{(L)}} = \dfrac{W_B}{M_B V_{(L)}}$

Normality $(N) = \dfrac{\text{Gram Equivalents}_{(B)}}{V_{(L)}} = \dfrac{W_B}{GEM_{(B)} \times V_{(L)}}$

Normality $= \text{Molarity} \times \dfrac{M_B}{GEM_{(B)}}$

Molarity $= \dfrac{d_{(Solution)} \times \text{Mass } \% \times 10}{M_B}$

Molality $(m) = \dfrac{n_B \times 1000}{W_A} = \dfrac{W_B \times 1000}{M_B W_A}$

$$x_A = \frac{n_A}{n_A + n_B} = \frac{W_A/M_A}{W_A/M_A + W_B/M_B}; \quad x_B = \frac{n_B}{n_A + n_B} = \frac{W_B/M_B}{W_A/M_A + W_B/M_B}$$

Colligative properties solutes which donot associate or dissociate

$$\Delta P/P^\circ = \frac{P^\circ - P}{P} = x_B$$

$$\Delta T_b = \frac{k_b W_B \times 1000}{M_B W_A}$$

$$\Delta T_f = \frac{k_f W_B \times 1000}{M_B W_A}$$

$$\pi = \frac{W_B RT}{M_B V}$$

$$K_b = \frac{R M_A T_b^2}{1000\, \Delta H_{vap.}}$$

Solutes undergoing association or dissociation in solution

$$\Delta P/P^\circ = \frac{P^\circ - P}{P} = i x_B$$

$$\Delta T_b = \frac{i k_b W_B \times 1000}{M_B W_A}$$

$$\Delta T_f = \frac{i k_f W_B \times 1000}{M_B W_A}$$

$$\pi = \frac{i W_B RT}{M_B V}$$

$$K_f = \frac{R M_A T_f^2}{1000\, \Delta H_{fus}}$$

$$i = \frac{\text{Normal mol. mass}}{\text{Observed mol. mass}} = \frac{\text{Observed colligative property}}{\text{Normal colligative property}}$$

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Degree of dissociation $(\alpha) = \frac{i-1}{m-1}$

Degree of association $(\alpha) = \frac{i-1}{1/m-1}$

EXERCISE

VERY SHORT ANSWER QUESTIONS
(1 Mark)

1. What is meant by pentimolar and semimolar solutions ?
2. What is meant by the statement that given solution is 0.4 M ?
3. Which out of molarity and molality changes with temperature and why ?
4. What is the normality of 0.3 M aqueous solution of a tribasic acid ?
5. A beaker contains 200 cm^3 of 0.1 M NaOH solutions. How many moles of NaOH are left in the solution when 50 ml of the solutions have been removed ?
6. What is Henry's law ?
7. What is the effect of rise in temperature on solubility of a gas ?
8. $\Delta H_{Sol.}$ of NH_4Cl is > 0, what is the effect of temperature on its solubility ?
9. What happens to the vapour pressure of water when some table salt is dissolved in it ?
10. Write the mathematical expression for Raoults law for the aqueous solution of non-volatile solute.
11. What is a semi-permeable membrane ? Given examples.
12. Why $CaCl_2$ is used to clear snow on roads ?
13. What is the effect of temperature on osmotic pressure ?
14. What are isotonic solutions ?
15. Write the Vant Hoff equation for dilute solutions.
16. How is the value of a colligative property related to molecular mass of the non-volatile solute ?
17. Why the use of pressure cooker reduces cooking time ?
18. What is reverse osmosis ? Describe its application ?
19. Why lowering of vapour pressure is not a colligative property ?
20. $CaCO_3$ shell is removed from the two eggs by treatment with dil. HCl. One of the egg is, then, placed in pure water while the other is saturated solution of NaCl. What will be observed and why ?
21. Four solutions, (A) 6% glucose, (B) 6% urea (C) 6% sucrose and (D) 6% Benzamide were subjected to freezing point measurement. Whose freezing point should be maximum ?
22. What type of substance generally show deliquescence ?
23. Give one practical application of depression of freezing point in automobiles.
24. Can we separate the components of azeotropic mixture by distillation.

DESCRIPTIVE QUESTIONS
(2—3 Marks)

Solutions and expressing concentration

25. What is a solution? Discuss various types of solutions.

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26. Differentiate between *solute* and *solvent* in a binary solution.
27. Explain the following terms with suitable examples as applied to solutions :
    (*i*) Molality (*ii*) Molarity (*iii*) Mole fraction.
28. Explain the terms molality and formality clearly indicating the difference between the two.
29. What is the effect of temperature on
    (*i*) Molarity (*ii*) Molality (*iii*) Mole fraction.
30. Describe the relationship between
    (*i*) Normality and molarity (*ii*) Molarity and molality.
31. Discuss giving examples the terms
    (*i*) Mass fraction (*ii*) Parts per million and mass %.

Vapour Pressure of Solution and Raoults law

32. What is the effect of the following on vapour pressure of the liquid
    (*i*) Nature of liquid (*ii*) Temperature.
33. Two liquids X and Y have boiling points 110°C and 130°C respectively. Which of them has lower vapour pressure at a given temperature ?
34. What happens when a system of liquid and vapour in equilibrium is
    (*i*) cooled (*ii*) heated
35. What is Raoult's law ? Give its mathematical expression.
36. State and explain Raoults law. ***(Haryana Board 1988)***
37. What is the vapour pressure of a liquid ? What is the effect of non-volatile solute on the vapour pressure of the liquid ?
38. What is meant by vapour pressure of a liquid ? What is the effect of temperature and size of the vessel on the vapour pressure of the liquid ?
39. What do you understand by relative lowering of vapour pressure of a solution ? How is it related to the concentration of the solute in the solution ?
40. Give two differences between lowering of vapour pressure and relative lowering of vapour pressure.

Ideal and Non-ideal Solutions

41. What is an ideal solution ? What type of solutions are likely to behave as ideal solutions ?
42. What are non-ideal solutions ? When does a solution exhibit positive deviation from ideality ?
43. Mixing acetone with chloroform takes place with reduction in volume. What type of deviation from Raoult's law is shown in this case and why ?
44. When X and Y are mixed the solution becomes warmer and when Y and Z are mixed the solution becomes cooler ? Which of these solutions will exhibit positive deviation and which will exhibit negative deviation ?
45. What are ideal and non-ideal solutions ? What type of non-idealities are exhibited by cyclohexane-ethanol and acetone-chloroform mixtures ? Give reasons for your answers. ***[A.I. CBSE (O) 1991]***
46. Explain along with diagrams that why some of non-ideal solutions show positive deviations while some other show negative deviations from ideal solutions. ***(Pb. 1991)***
47. What are azeotropes ? Give one example each of minimum boiling and maximum boiling azeotrope.

Colligative properties

48. What are colligative properties ? Show that relative lowering of vapour pressure is a colligative property.
49. What is molal elevation constant ? What are its units ?
50. Explain with the help of vapour pressure curves why a solution containing non-volatile solute has higher boiling point than the pure solvent.
51. How will you determine the molecular mass of a non-volatile substance by study of elevation in boiling point of a solution ?

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52. Why common salt is added to water used for boiling eggs to get hard boiled eggs ?
53. Explain with the help of vapour pressure curves why freezing point of a liquid is lowered when some non-volatile solute is dissolved in it.
54. Derive the relationship between depression of freezing point and the molality ?
55. What is molal depression constant ? What are its units ?
56. What are antifreeze solutions ? Which substance is commonly used as antifreeze ?
57. Why do you sometimes get abnormal molecular masses of substances ? Give modified equations for the colligative properties for substances exhibiting abnormal molecular masses. *(CBSE 1992)*
58. Why is freezing point of H_2O lowered on adding NaCl whereas its boiling point is elevated ? How are these properties used for determining molecular masses ?
59. Explain the following terms :
    (*i*) Osmosis (*ii*) Osmotic pressure (*iii*) Semi-permeable membrane.
60. Define osmotic pressure. Arrange the following solutions in the increasing order of their osmotic pressure :
    (*a*) 34.2 gm/lit sucrose (*b*) 60 gm/lit urea $H_2N.CO.NH_2$
    (*c*) 90 gm/lit glucose (*d*) 58.5 gm/lit sodium chloride
    Give reason in support of your answer. *[Har. (Sc.) 1992]*
61. What is osmotic pressure ? Show that it is a colligative property.
62. Describe a method for the determination of osmotic pressure.
63. Differentiate between osmosis and diffusion.
64. How will you determine the molecular mass of a non-volatile substance by study of osmotic pressure ?
65. What is the effect of the following changes on the osmotic pressure of a solution containing non-volatile solute ?
    (*i*) Solvent is added to the solution. (*ii*) Solute is added to the solution.
    (*iii*) Temperature is raised.
66. When fruits and vegetables that have dried are placed in water, they slowly swell. Explain why ? What would be the effect of temperature on this process ?
67. Explain giving examples why sometimes abnormal molecular masses of the substances are obtained by using the colligative properties of the solutions.
68. What is Van't Hoff's factor ? How is it related to degree of dissociation of the electrolyte in the solution ? What is its value when the solute undergoes association ?
69. Mention three characteristics of ideal solutions. What causes deviations from ideal behaviour ? Discuss positive deviation and negative deviation from ideal behaviour for liquid pairs. *[CBSE (2) 1992]*
70. How does a non-ideal solution differ from an ideal solution ? What does positive deviation occur from ideality ?
71. What is osmotic pressure ? How will you determine the molar mass of substance by this method ? *[Har. (Sc.) 1988]*
72. What is osmotic pressure ? How will you determine the molecular mass of substance with a method based on it ? Why is this method preferred for measuring molecular masses of macromolecules ? *[CBSE (4) 1992]*
73. Which colligative property is preferred for molar mass determination of polymers or macromolecular substances and why ?
74. What care is generally taken during intravenous injection and why ?
75. Which out of 1 molar and 1 molal aqueous solution is more concentrated and why ?

NUMERICAL PROBLEMS

76. 250 ml of 0.2 M K_2SO_4 solution is mixed with 250 ml of 0.2 M KCl solution. What is the molar concentration K^+ ions in the resulting solution ? *(BIT Ranchi 1991)*

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77. 20 g of a non-volatile solute is dissolved in 100 g of water at 298 K. The vapour pressure is lowered from 23.76 to 22.41 mm of Hg. Calculate

(*i*) ΔP (*ii*) $\Delta P/P^\circ$

(*iii*) n_B (*iv*) nM_B.

78. If glycerol and glycol were sold at the same price per kg, which would be cheaper for preparing the antifreeze solution for the car radiator ?

79. The boiling point of a solution containing 0.5 g of solute B (molar mass 0.128 kg mol^{-1}) per 50 g of solvent is raised by 0.4 K while 0.6 g of another solute C raises the boiling of 50 g of same solvent by 0.6 K calculate the molar mass of solute C.

80. A solution containing 30 g of a non-volatile solute in exactly 90 g of water has vapour pressure of 21.85 mm Hg at 25°C. Further, 18 g of water is then added to the solution. The vapour pressure of resulting solution is 22.15 mm Hg at 25°C. Calculate mol. mass of solute and vapour pressure of water.

81. Show that for a aqueous solution of solute A with mol. mass W, the molarity M and molality *m* are related as

$$\frac{d}{M} = \frac{1}{m} + \frac{W}{1000}.$$

82. An acid with molecular mass 300 is dissolved in water to prepare 0.1 M solution having density 1.01 gm/cm^3. If acid is 4.5% ionised. Calculate freezing point of the solution (k_f = 1.86 kg mol^{-1}).

83. In cold climate water gets frozen causing damage to the car radiator. Ethylene glycol is used as antifreeze agent calculate the amount of ethylene glycol to be added to 4 kg of water to prevent if from freezing at – 6°C. *(Rookee 1992)*

84. What mass of urea need to be dissolved in 100 g of water in order to decrease its vapour pressure by 25% ? What will be the molality of the solution ? *(I.I.T. 1993)*

85. Calculate freezing point of an aqueous solution of a non-electrolyte having osmotic pressure of 2.0 atm at 300 K (k_f = 1.86 K kg mol^{-1} , R = 0.0821 L atm K^{-1} mol^{-1}). *(Rookee 1993)*

86. 8.0575×10^{-2} kg of Glauber's salt is dissolved in water to obtain 1 dm^3 of solution of density 1077.2 kg m^{-3}. Calculate molarity, molality and mole fraction of Na_2SO_4 in solution. *(I.I.T. 1994)*

87. The freezing point of a solution contain 0.2 g of acetic acid in 20.0 g of benzene is lowered by 0.45°C. Calculate degree of association of acetic acid in benzene (k_f for benzene is = 5.12 K kg mol^{-1}). *(Rookee 1994)*

88. Calculate the amount of ice that will separate out on cooling the solution containing 50 g of ethylene glycol, $(CH_2OH)_2$ in 200 g of water at – 9.3°C (k_f for water = 1.86 K kg mol^{-1}). *(Rookee 1995)*

89. Calculate the boiling point of a 1 molar aqueous solution (density = 1.04 gL^{-1} of KCl (k_b for water 1.52 K kg mol^{-1}). *(CBSE 1995)*

90. 0.85% aqueous solution of $NaNO_3$ is apparently 90% dissociated at 27°C. Calculate the osmotic pressure. (R = 0.082 L-atm K^{-1} mol^{-1}). *(Rookee 1996)*

91. The molar volume of liquid benzene (d = 0.877 g mol^{-1}) is increased by a factor of 2750 as it vaporises at 20°C and that of liquid toluene (d = 0.867 g mol^{-1}) increased by a factor of 7720 at 20°C. A solution of benzene and toluene at 20°C has V.P. of 46.0 torr. Find the mole fraction of benzene in the vapour above the solution. *(I.I.T. 1996)*

92. A small amount of a non-volatile solute that does not dissociate is dissolved in 56.8 cm^3 of benzene (d = 0.889 g mol^{-1}). At room temperature, the vapour pressure of this solution is 98.88 mm of Hg while that of benzene is 100 mm Hg. Find the molality of this solution. If freezing temperature of this solution is 0.73 degree lower than that of benzene. What is the value of molal depression constant of benzene ? *(I.I.T. 1997)*

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FOR THE COMPETITIVE EXAMS

MULTIPLE CHOICE QUESTIONS

Select the correct answers from the four alternatives in each of the following :

1. Which one of the following is not a colligative property ?
   (*a*) Optical activity (*b*) Osmotic pressure
   (*c*) Depression of freezing point (*d*) Elevation of boiling point.
2. Determination of correct mol. mass from Raoult's Law is applicable to
   (*a*) an electrolyte in solution (*b*) a non-electrolyte in a dilute solution
   (*c*) a non-electrolyte in a concentrated solution (*d*) an electrolyte in a liquid solvent.
3. The flow of solvent through a semi-permeable membrance towards the solution side is the phenomenon of
   (*a*) adsorption (*b*) diffusion (*c*) osmosis (*d*) transfusion.
4. Semi-permeable membrane allows
   (*a*) a solution to pass through it (*b*) solute to through it
   (*c*) solvent to pass through it (*d*) both the solute and solvent to pass through it.
5. If $p°$ and p are the vapour pressures of a solvent and its solution respectively and N_1 and N_2 are the mole fractions of the solvent and solute respectively, then
   (*a*) $p = p°N_1$ (*b*) $p = p°N_2$ (*c*) $p° = pN_2$ (*d*) $p = p°(N_1/N_2)$.
6. For a dilute solution, Raoult's law states that
   (*a*) the lowering of vapour is equal to the mole fraction of solute
   (*b*) the relative lowering of vapour pressure is equal to the mole fraction of solute
   (*c*) the relative lowering of vapour pressure is proportional to the amount of solute in solution
   (*d*) the vapour pressure of the solution is equal to the mole fraction of the solvent. ***(I.I.T., 1985)***
7. Properties which depend on the number, rather than the nature of the dissolved particles in a solution are called
   (*a*) general (*b*) colligative (*c*) isotropic (*d*) isotonic.
8. A molal solution is one that contains one mole of a solute in
   (*a*) 1000 g of the solvent (*b*) one litre of the solvent
   (*c*) one litre of the solution (*d*) 22.4 litres of the solution. ***(I.I.T., 1986)***
9. Choose the correct statement. For a solution containing non-volatile solute
   (*a*) vapour pressure of a solution is equal to that of the solvent
   (*b*) vapour pressure of a solution is less than that of a solvent
   (*c*) vapour pressure of a solution is more than that of a solvent
   (*d*) none of the above.
10. The number of moles of solute present in 1000 g of the solvent is known as
    (*a*) molarity (*b*) molality (*c*) normality (*d*) mole fraction.
11. In which mode of expression, the concentration of a solution remains independent of temperature ?
    (*a*) Molarity (*b*) Normality (*c*) Formality (*d*) Molality. ***(I.I.T., 1988)***
12. The osmotic pressure increases, if
    (*a*) temperature is decreased (*b*) concentration of solute is increased
    (*c*) concentration of solute is decreased (*d*) volume of solution is increased.

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13. The osmotic pressure of a solution is directly proportional to
(*a*) the molecular concentration of the solute (*b*) the absolute temperature at a given concentration
(*c*) the lowering of vapour pressure (*d*) all of the above.

14. Isotonic solutions are the solutions of same
(*a*) surface tension (*b*) concentration (*c*) osmotic pressure (*d*) viscosity.

15. Which of the following is a colligative property ?
(*a*) osmotic pressure (*b*) boiling point (*c*) vapour pressure (*d*) electrical conductivity.

16. Which of the following solutions have highest freezing point ?
(*a*) 0.1 M NaCl (*b*) 0.1 M $BaCl_2$ (*c*) 0.1 M $Al_2(SO_4)_3$ (*d*) 0.1 M urea.

17. Which of the following 0.1 M aqueous solutions will have the lowest freezing point ?
(*a*) potassium sulphate (*b*) sodium chloride (*c*) urea (*d*) glucose. ***(I.I.T., 1989)***

18. The mass of $((COOH)_2 . 2H_2O)$ needed to prepare 500 ml of 0.1 molar solution is
(*a*) 12.6 gm (*b*) 6.3 gm (*c*) 4.5 gm (*d*) 9.0 gm.

19. Which of the following solutions has highest osmotic pressure ?
(*a*) 1 M NaCl (*b*) 1 M urea (*c*) 1 M sucrose (*d*) 1 M glucose.

20. Which of the following solutions (in water) has highest boiling point ?
(*a*) 1 M NaCl (*b*) 1 M $MgCl_2$ (*c*) 1 M urea (*d*) 1 M glucose.

21. Which of the following aqueous solutions containing 10 g of solute in each case, has highest m.pt. ?
(*a*) NaCl solution (*b*) KCl solution (*c*) sugar solution (*d*) glucose solution.

22. Equal volumes of 0.1 M $AgNO_3$ and 0.2 M NaCl solutions are mixed. The concentration of NO_3^- ions in mixture solution will be
(*a*) 0.1 M (*b*) 0.05 M (*c*) 0.2 M (*d*) 0.15 M.
(Pb. PMT 1994 ; BHU 1994)

23. The molal freezing point constant for water is $1.86°CM^{-1}$. The freezing point of 0.1 m NaCl solution is expected to be
(*a*) – 1.86°C (*b*) – 0.372°C (*c*) – 0.186°C (*d*) 0.372°C. ***(MLNR 1994)***

24. The solution containing 6.8 g of non-ionic solute 100 g of water was found to freeze at – 0.93°C. If K_f for water is 1.86, the mol. mass of solute is
(*a*) 13.6 (*b*) 68 (*c*) 34 (*d*) 136. ***(Pb. PMT 1994)***

25. In case of electrolyte which dissociates in solution the Van't Hoff's factor, *i* is
(*a*) > 1 (*b*) < 1 (*c*) = 1 (*d*) = 0.

26. Which of the following salt will have same value of Vant Hoff's factor (*i*) as that of $K_4[Fe(CN)_6]$
(*a*) $Al_2(SO_4)_3$ (*d*) NaCl (*c*) $Al(NO_3)_3$ (*d*) Na_2SO_4.
(CBSE Med. Ent. 1994)

27. 120 g of urea is present in 5 L of solution, the active mass of urea is
(*a*) 0.2 (*b*) 0.06 (*c*) 0.4 (*d*) 0.8. ***(CET MP 1994)***

28. Which of the following behaviour is true about ideal binary liquid solution ?
(*a*) Plot of P_{Total} *vs* X_A is non-linear (*b*) Plot of P_{Total} *vs* X_B is linear
(*c*) Plot of P_{Total} *vs* X_B is linear with slope = 0 (*d*) Plot of P_{Total} *vs* X_A is linear with slope = 0.

29. The increase in the temperature of the aqueous solution will result in its
(*a*) Molarity to increase (*b*) Molarity to decrease
(*c*) Mole fraction to increase (*d*) Mass % to increase. ***(ISM Dhanbad 1994)***

30. The osmotic pressure of 5% aqueous solution of sugar (mol. mass 342) at 15°C is
(*a*) 4 atm (*b*) 3.45 atm (*c*) 3.55 atm (*d*) 2.45 atm.
(BHU Med. Ent. 1995)

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31. Which of the following 0.1 m aqueous solution will have the lowest freezing point ?
(*a*) $Al_2(SO_4)_3$ (*b*) $C_5H_{10}O_5$ (*c*) KI (*d*) $C_{12}H_{22}O_{11}$.
(*CBSE Med. 1997*)

ASSERTION REASON TYPE QUESTIONS

The following questions contain two statements, one labbled as ***Assertion* A** and the other labbled as ***Reason* R**. Examine both the statements and mark the correct choice *a, b, c* or *d* according to the instruction given below.

(*a*) If both A and R are correct and R is reason of A

(*b*) If both A and R are correct but R is not correct reason of A

(*c*) If A is correct R is wrong

(*d*) If A is wrong R is correct.

32. ***Assertion* A :** A molar solution always more concentrated than molar solution.
***Reason* R :** A molar solution contains one mol of solute in 1000 ml of solution.
(*a*) (*b*) (*c*) (*d*)

33. ***Assertion* A :** Molarity of 0.02 N solution of HNO_3 is 0.02 M.
***Reason* R :** Molarity and normality of a solution are always equal.
(*a*) (*b*) (*c*) (*d*)

34. ***Assertion* A :** Two solutions having same osmotic pressures will also have same vapour pressures.
***Reason* R :** Lowering of vapour pressure is not a colligative property.
(*a*) (*b*) (*c*) (*d*)

35. ***Assertion* A :** Cooking time is reduced in pressure cooker.
***Reason* R :** Boiling point of water inside the pressure cooker is elevated.
(*a*) (*b*) (*c*) (*d*)

36. ***Assertion* A :** 0.02 m solutions of urea and sucrose will freeze at same temperature.
***Reason* R :** Freezing point of a solution is inversely portional to the conc. of solution.
(*a*) (*b*) (*c*) (*d*)

FILL IN THE BLANKS

Fill in the blanks with appropriate items :

1. Molality of the solution is number of moles of the solute in each ..... kg of .....
2. The ratio of the number of moles of solvent to the total number of moles of solute and solvent is called .....
3. The molarity of the solution of non-electrolyte at 0°C if its osmotic pressure is 17 mm is approx. .....
4. The properties of the solution which depend upon the concentration of solute particles are called .....
5. The boiling point of sea water at 1 atm pressure is ..... that of distilled water.
6. A solution which does not obey Raoult's law at all range of concentration is called .....
7. Molal cryoscopic constant depends upon .....
8. The ratio of observed value of colligative property to the calculated value of colligative property is called .....
9. The evaporation of aqueous solution of glucose causes its molarity to .....
10. The molarity and normality of an aqueous solution of oxalic acid dihydrate are related as .....
11. A solution which distils without change in composition is called .....

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12. Relative lowering of vapour pressure is equal to the mole fraction of the .....
13. For an ideal solution ΔH_{mixing} is .....
14. ..... solutions have same osmotic pressure.
15. For sodium chloride solution Van't Hoff's factor '*i*' is .....
16. Every solution behaves as ideal solution if ,..... (*MLNR 1995*)

TRUE/FALSE STATEMENTS

Mark the following statements as true or false :

1. The sum X_B and X_A in binary solution is > unity.
2. The value of ΔS_{mix} for ideal solution is = 0.
3. ΔG_{mix} for ideal solution should be < 0.
4. Molarity is the number of moles of solute dissolved per litre of the solution.
5. If pressure greater than osmotic pressure is applied on solution which has been separated from pure solvent by semi-permeable membrane reverse osmosis will occur.
6. The freezing point of impure water is greater than that of pure water at particular pressure.
7. Both lowering of vapour pressure and relative lowering in vapour pressure are colligative properties.
8. A 10% aqueous solution of NaCl is isotonic with 10% aqueous solution of glucose.
9. Water boils at a lower temperature at higher altitudes.
10. Determining mol. mass of polymers by measuring osmotic pressure is not a suitable method.
11. For solution of acetic acid in benzene '*i*' greater than 1.
12. Molarity of a solution changes with temperature.
13. All solutions obey Raoult's law.
14. Osmotic pressure is directly proportional to temperature.
15. All solutions containing 1 g of non-volatile solutes will have same freezing point.

MATCHING THE COLUMNS

Match the items of column A, B and C :

A	B	C
1. Depression produced in the freezing point of water when 60 g of urea is dissolved in 1 kg of it	(1) *i*	(1) Molarity
2. Relative lowering of vapour pressure	(2) k_f	(2) Solutions with same composition of vapour above it
3. $\frac{n_{(solute)}}{V_{soln.}(L)}$	(3) Solutions with same osmotic pressure	(3) $\frac{\text{Observed Mol. mass}}{\text{Theoretical Mol. mass}}$
4. Constant boiling mixtures	(4) $\frac{P^\circ - P}{P^\circ}$	(4) Isotonic solution

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A	B	C
5. 1 M solution of glucose and 1 M solutions of sucrose	(5) One of mode of expressing concentration of solution	(5) Quantity equal to mole fraction of solute
6. Vant Hoff factor	(6) Azeotrope	(6) Molal cryoscopic constant

ANSWERS AND HINTS

REVIEW PROBLEMS

3.1. 0.189 N

3.2. 0.0697, 4.163 mol^{-1} kg, 3.417 mol L^{-1}

3.3. 6.337 mol kg^{-1}, 0.1024

3.4 0.503, 0.196, 0.301

3.5. 1 N, 0.943 m

3.6. 200 ml

3.7. 0.45 M

3.8. 0.25 M

3.9. (*i*) 0.56 m (*ii*) 0.099

3.10. 1.68 M, 1.8 m

3.11 0.02 m

3.12. 0.5 N

3.13. 8.89 M, 11.39 m

3.14. $X_A = 0.982$; $X_B = 0.118$

3.15. 10^{-2} cm^3

3.16. (*i*) 0.065 ; (*ii*) Na^+ = 7.730 m, (*iii*) $S_2O_3^{2-}$ = 3.865 m

3.17. 0.037

3.18. 0.20 m ; 0.235 M

3.19. (*i*) 0.656 M, (*ii*) 50 mill moles

3.20. 86.76 cm^3

3.21. 0.8

3.22. $P_A° = 450$ torr ; $P_B° = 150$ torr

3.23. 0.2

3.24. (*i*) 0.74 ; (*ii*) 0.0132

[**Hint.** V.P. of pure water at 373 K (b.p.) is 760 mm

$\therefore$ $\Delta P = 760 - 750 = 10$ mm

$\Delta P/P_A°$ = mole fraction of solute

Let total number of moles = 1

$\therefore$ $n_{solute} = 0.0132$; $n_{solvent} = 0.9868$

Mass of solvent $= 0.9868 \times 18$ g]

3.25. Urea = 0.025 ; Ethanol = 0.975

3.26. 758.28 m

3.27. 388 torr

3.28. 19.81 torr

3.29. 23.375 mm of Hg

3.30 55.81 $\left[\text{Hint. } \frac{\Delta P}{P_A°} = \frac{0.055}{0.9675} = 0.057 = \frac{W_B/M_B}{W_A/M_A}\right]$

3.31. 240

3.32. 0.6

3.33. 253

3.34. 373.0104 K

3.35. 183.9

3.36. 272.256 K

3.37. 344.4

3.38. 180

3.39. 451.12

3.40. S_8

3.41. 0.1113 moles

3.42. 0.1362×10^6 Nm^{-2}

3.43. 6190.4

3.44. (*i*) p = 17.4 mm ; (*ii*) π = 4.8 atm (*iii*) b.pt. = 373.104 K ; (*iv*) f.pt. = 272.628 K

3.45. 54093

3.46. 123000

3.47. 2.24 atm

3.48. 59.28 [**Hint.** $\pi_1 = \pi_2$ or $C_1RT = C_2RT$ or $n_1 = n_2$ or $W_1/M_1 = W_2/M_2$]

3.49. 6240

3.50. 58.06 g

3.51. 0.054 mol or 3.16 g

3.52. $i = 1.9$; $\alpha = 0.9$ or 90%

3.53. $\alpha = 0.95$; $i = 1.95$

3.54. (*i*) $O_2 = 4 \times 10^{-3}$ g ; (*ii*) $Ca^{2+} = 4.5 \times 10^{19}$

3.55. 4.20 atm [**Hint.** Find osmotic pressure of each solute in 200 ml of solution separately and add them]

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3.56. 50 g **3.57.** 19.19 M **3.58.** 156

3.59. (*i*) 0.30 mol L^{-1} (*ii*) – 0.558°C

3.60. 356 atm [**Hint.** Apply equation $\pi = \frac{\Delta P}{P_A^\circ} \times \frac{dRT}{M_B}$]

3.61. 4.20 atm.

Hint. Total volume after mixing = 200 ml. Now, find osmotic pressure due to urea (π_1 = 3 atm) and that due to sugar (π_2 = 1.2 at m) Add π_1 and π_2 to get final osmotic pressure.

VERY SHORT ANSWER QUESTIONS

1. Pentimolar means M/5 and semimolar means M/2.
2. This implies that 1 litre of solution contains 0.4 moles of solute.
3. Volume of the solution increases with rise in temperature, and this, brings changes in the molarity because it relates moles of solute and volume of solution.
4. Normality = Molarity × basicity = 0.3 × 3 = 0.9 N.
5. Remaining volume = 150 cm^3. Moles = $150 \times 10^{-3} \times 0.1 = 1.5 \times 10^{-2}$.
7. Gas + Water $\rightleftharpoons$ Solution ; ΔH = – ve. Dissolution of gas is exothermic process. Hence, according Le-Chatelier's principle, the solubility of gas should decrease by rise in temperature.
8. Since dissolution process is endothermic ∴ Solubility increases by rise in temperature.
10. $P = P_A^\circ x_A$ or $\frac{P_A^\circ - P}{P_A^\circ} = x_B$.
13. Osmotic pressure ∝ T.
15. $\pi V = nRT$.
16. Colligative property $\propto \frac{1}{\text{mol. mass}}$.
17. Because of higher pressure over the liquid (due to weight of the pressure cooker) the liquid boils at higher temperature and hence cooking takes place faster.
20. The egg placed in water will increase in size due to osmosis of pure water into the egg, while the other egg placed in NaCl solution, will shrink due to osmosis of water out of the egg.
21. 6% sucrose.
22. **Deliquescence** is a phenomenon by virtue of which a crystalline substance on standing in air forms a solution by absorbing water vapours from the atmosphere. For deliquescence to occur the substance should be very soluble in water and its saturated solution should have low vapour pressure as compared to the pressure of water vapours in air at particular temperature.
23. One of important application is use of antifreeze (solution of ethylene glycol) in radiators.
24. No, it is not possible to separate the contents of azeotropic mixture by distillation.

DESCRIPTIVE QUESTIONS

34. (*i*) A part of the vapours change into liquid and a new equilibrium is established. As a result v.p. of the liquid decreases.
    (*ii*) More of liquid changes into vapours and a new equilibrium is established. As a result v.p. of the liquid increases.
43. Negative deviation ; Decrease in volume of solution indicates strong forces of attraction between the molecules in solution.
44. X and Y—negative deviation ; Y and Z—positive deviation.
49. K kg mol^{-1}.
52. Addition of salt to water increases it b.p.
56. Ethylene glycol.

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65. (*i*) decreases (*ii*) increases (*iii*) increases.

66. Due to absorption of water through osmosis ; this process increases with increase in temperature.

73. Osmotic pressure measurement is preferred over other colligative properties for determining the mol. mass of polymers because

(*i*) Osmotic pressure is considerably high even in dilute solutions

(*ii*) Osmotic pressure can be measured at room temperature. Elevation in b.p. is measured at high temperature and may cause decomposition. While low temperature may also cause changes in extent of polymerisation.

74. During intravenous injection, the concentration of the solution should be approximately same as that of blood plasma so that they are isotonic. If solution to be injected is hypertonic it will cause cell to shrink. On the other hand if the solution to be injected is hypotonic, it will cause cells to burst.

75. A molar solution contains 1 mol of solute in 1000 ml of solution but one molal solution contains 1 mol of solute in 1000 g, *i.e.* 1000 ml of water assuming density to be one. Thus, in 1 molar solution one mole of solute is present in less than 1000 ml of water because total volume of solution is equal to 1000 ml. Thus 1 M aq. solution is generally concentrated. However, if density of solution is greater than one then, the 1 m aq. solution will be more concentrated.

76. Moles of K^+ ions in 250 ml of 0.2 M $K_2SO_4 = 2(0.2 \times 250 \times 10^{-3})$

Moles of K^+ ions in 250 ml of 0.2 M KCl $= 0.2 \times 250 \times 10^{-3}$

Total K^+ ions in 500 ml $= 3 \times 0.2 \times 250 \times 10^{-3}$

Conc. of K^+ ions $= \dfrac{3 \times 0.2 \times 250 \times 10^{-3} \times 10^3}{500} = \mathbf{0.3\ M.}$

77. $\Delta P = \mathbf{1.35\ mm\ of\ Hg}$; $\Delta P/P^\circ = \mathbf{0.0568}$; $n_B = \mathbf{0.3345}$; $M_B = \mathbf{59.8.}$

78. Glycol.

79. $k_b = \mathbf{5.12\ K.kg\ mol^{-1}}$; $M_C = \mathbf{102.4\ g\ mol^{-1}}$.

80. Vapour pressure of water = **23.65 mm of Hg** ; $M_{Solute} = \mathbf{44}$

82. $CH_3COOH \rightleftharpoons CH_3COO^- + H^+ \quad \therefore \quad m = 2$

$$\alpha = 0.045 \qquad \therefore \quad \frac{i-1}{2-1} = 0.045 \text{ or } i = \mathbf{1.045}$$

Mass of 1 L of solution $= 1000 \times 1.01 = 1010$ g

0.1 Mol of acetic acid $= 6$ g

$\therefore$ Mass of solvent $= 1010 - 6 = 1004$ g

$$\Delta T_f = i\,k_f \frac{n \times 1000}{W_A} = \frac{1.045 \times 1.86 \times 0.1 \times 1000}{1004} = 0.1935$$

$\therefore$ Freezing point $= \mathbf{-0.193°C.}$

83. $W_B = \dfrac{M_B \times W_A \times \Delta T_f}{1000 \times k_f} = \dfrac{62 \times 4\,(kg) \times 6}{1000 \times 1.85} = \mathbf{0.804\ kg}$

84. $\dfrac{\Delta P}{P^\circ} = \dfrac{25}{100}$, $W_A = 100$ g; $W_B = ?$, $M_B = 60$; $M_A = 18$

$$\frac{\Delta P}{P^\circ} = \frac{W_B/M_B}{W_B/M_B + W_A/M_A} \text{ or } W_B = \mathbf{111.11\ g}$$

85. $\pi = CRT$ or $C = \pi/RT = \dfrac{2}{0.0821 \times 300} = 0.0812$ M

Assume 0.0812 M $\approx$ 0.0812 *m* for their solution

$\therefore \quad \Delta T_f = k_f \times m = 1.86 \times 0.0812 = 0.151°C$

Thus, freezing point is **– 0.151°C.**

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86. Moles of Na_2SO_4 in 1 dm^3 solution $= \dfrac{8.0575 \times 10^{-2} \times 10^3 \text{ (g)}}{142 \text{ (GMM)}} = 0.567$ mol

$\therefore$ Molarity of solution = **0.567 M**

Mass of solution $= 1 \text{ dm}^3 \times 1077.2 \text{ kg m}^{-3} = 10^{-3} \text{ m}^3 \times 1077.2 \text{ kg m}^{-3} = 1.0772$ kg

Mass of solvent $= 1.0772 \text{ kg} - 0.080575 \text{ kg} = 0.0996625$ kg

Molality of solution $= \dfrac{0.567 \text{ mol}}{0.996625 \text{ kg}} =$ **0.569 m**

Moles of solvent $= \dfrac{0.996625 \times 10^3 \text{ (g)}}{18} = 55.37$

$$X_{Na_2SO_4} = \frac{0.567}{0.567 + 55.37} = \mathbf{0.01}$$

87. ΔT_f(Theoretical) $= \dfrac{1000 \times 5.12 \times 0.2}{20 \times 60} = 0.853°$

ΔT_f(Obs.) = 0.45°

$$i = \frac{0.45}{0.853} = 0.528$$

$$2CH_3COOH \longrightarrow (CH_3COOH)_2$$

$\therefore$ $\alpha_{association} = \dfrac{i-1}{1/m-1} = \dfrac{0.528-1}{1/2-1} = \dfrac{-0.472}{-0.5} =$ **0.944** or **94.4%**

88. $\Delta T_f = k_f \cdot \dfrac{W_B \times 1000}{M_B \times W_A}$ or $W_A = k_f \dfrac{W_B \times 1000}{M_B \times \Delta T_f} = \dfrac{1.86 \times 50 \times 1000}{58 \times 9.3} = 172.41$ g

$\therefore$ Amount of ice that will separate = 200 – 172.41 = **27.59 g.**

89. Mass of 1 L of solution $= 1000 \text{ (ml)} \times 1.04 \text{ g ml}^{-1} = 1040$ g

Mass of one mol of KCl = 74.5 g

Mass of solvent (W_A) = 1040 – 74.5 = 965.5 g

$$\Delta T_b = \frac{0.52 \times 74.5 \times 1000}{74.5 \times 965.5} = 0.538°$$

$\therefore$ Boiling point = 100 + 0.538 = **100.538°C.**

90. $NaNO_3 \rightleftharpoons Na^+ + NO_3^-$; $\alpha = 0.90$

Now, $\alpha = \dfrac{i-1}{m-1} = \dfrac{i-1}{2-1} = i - 1$ or $i = 1 + \alpha = 1 + 0.90 = 1.90$

$$\pi = i\,CRT = 1.90 \times \frac{0.85}{85} \times \frac{1000}{100} \times 0.082 \times 300 = \mathbf{4.674 \text{ atm}}$$

91. Volume of 1 mole of liquid benzene $= \dfrac{78}{0.877} = 88.94$ ml

Volume of 1 mol of benzene vapour = 88.94 × 2750 ml = 244.585 L

V.P. of pure benzene at 20°C ($P_b°$) $= \dfrac{RT}{V} = \dfrac{0.082 \times 293}{244.585} = 0.098$ atm

Volume of 1 mole of liquid toluene $= \dfrac{92}{0.867} = 106.113$ ml

Volume of 1 mol of toluene vapour = 106.113 × 7720 ml = 819.192 L

V.P. of pure toluene at 20° ($P_t°$) $= \dfrac{0.082 \times 293}{81.9192} = 0.029$ atm

Now, $P_b = x_b \times P_b° = x_b \times 0.098$

$P_t = x_t \times P_t° = (1 - x_b) \times 0.029$

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$$P_{total} = P_b + P_t = x_b \times 0.098 + (1 - x_b) = 0.029 = \frac{46}{740} = 0.06 \text{ atm}$$

$\therefore$ $x_b = 0.449$

Mole fraction of benzene in vapour $= \frac{P_b}{P_{total}} = \frac{x_b + P_b^\circ}{0.06} = \frac{0.449 \times 0.098}{0.06} = \mathbf{0.73}$

92. Mass of benzene $= 56.8 \times 0.889 = 50.49$ g

$P_{sol.} = 98.88$ mm $\quad P^\circ_{benzene} = 100$ mm $\quad \therefore \frac{\Delta P}{P^\circ} = \frac{100 - 98.88}{100} = \frac{1.12}{100}$

Now, $\frac{\Delta P}{P^\circ} = \frac{W}{M} \times \frac{M_{benzene}}{W_{benzene}}$

or No. of moles of solute (W/M) $= \frac{\Delta P}{P^\circ} \times \frac{W_{benzene}}{M_{benzene}} = \frac{1.12 \times 50.40}{100 \times 78} = 0.0072$

Mole of solute in 1000 g of benzene, *i.e.* molality $= \frac{0.0072}{50.49} \times 1000 = \mathbf{0.142\ m}$

Now, $\Delta T = m \times k_f$ or $k_f = \frac{\Delta T}{m} = \frac{0.73}{0.142} = \mathbf{5.14\ kg\ K^{-1}\ mol^{-1}}$.

MULTIPLE CHOICE QUESTIONS

1. (*a*)	**2.** (*b*)	**3.** (*c*)	**4.** (*c*)	**5.** (*a*)	**6.** (*b*)
7, (*b*)	**8.** (*a*)	**9.** (*b*)	**10.** (*b*)	**11.** (*d*)	**12.** (*b*)
13. (*d*)	**14.** (*c*)	**15.** (*a*)	**16.** (*d*)	**17.** (*a*)	**18.** (*b*)
19. (*a*)	**20.** (*b*)	**21.** (*c*)	**22.** (*b*)	**23.** (*c*)	**24.** (*d*)
25. (*a*)	**26.** (*a*)	**27.** (*c*)	**28.** (*b*)	**29.** (*b*)	**30.** (*b*)
31. (*a*)	**32.** (*d*)	**33.** (*d*)	**34.** (*c*)	**35.** (*a*)	**36.** (*c*)

FILL IN THE BLANKS

1. one, solvent	**2.** mole fraction of solvent	**3.** 0.1 M
4. colligative properties	**5.** greater than	**6.** non-ideal solution
7. nature of solvent	**8.** Vant Hoff factor	**9.** increase
10. Normality = 2 × Molarity	**11.** azeotrope	**12.** solute
13. zero	**14.** Isotonic	**15.** greater than 1
16. it obeys Raoult's law.		

TRUE/FALSE STATEMENT

1. False	**2.** False	**3.** True	**4.** True	**5.** True	**6.** False
7. False	**8.** False	**9.** True	**10.** False	**11.** False	**12.** True
13. False	**14.** True	**15.** False			

MATCHING THE COLUMNS

1—2—6 ; 2—4—5 ; 3—5—1 ; 4—6—2 ; 5—3—4 ; 6—1—3

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4

Chemical Thermodynamics

LEARNING OBJECTIVES

- ***First Law of thermodynamics*** *: Internal energy, enthalpy, Application of first law of thermodynamics.*
- ***Second Law of thermodynamics*** *: Entropy, Free energy, spontaneity of chemical reactions ; Free energy change and chemical equilibrium. Free energy as energy available for useful work.*
- ***Third law of thermodynamics.***

Thermodynamics, literally, means conversion of heat into work and *vice versa*. The name was originally devised by mechanical engineers who were interested in the conversion of heat into work because **therm** refers to *heat* and **dynamics** refers to *movement*. Now-a-days the term thermodynamics is used in much wider sense as it deals with almost all forms of energies. **Thermodynamics** may, therefore, be defined as :

the branch of science which deals with the quantitative relationship between heat and other forms of energies.

When we confine our study to thermodynamics of chemical processes, it is referred to as **chemical thermodynamics.**

Thermodynamics is primarily based upon three fundamental generalisations which have been arrived at purely on the basis of human experience. These generalisations are called First, Second and Third Laws of thermodynamics. The predictions based upon these laws have been verified in most of the cases and so far no case has been reported where these laws break down. In general,

First Law deals with the equivalence of different forms of energies.

Second Law deals with the direction of chemical change.

Third Law helps to evaluate the thermodynamics parameters like entropy.

Scope and Limitations of Thermodynamics

The **importance** of thermodynamics lies in its ability to predict

(*i*) the feasibility of the chemical reaction under the given set of conditions and

(*ii*) the extent to which the chemical reaction can occur before the equilibrium is attained.

The significant **limitations** of thermodynamics include its failure to tell about :

(*i*) the speed or rate of the reaction,

(*ii*) the mechanism of the reaction and its inability to be applied to microscopic systems such as individual atoms and molecules.

Before we take up the study of these laws and other thermodynamic parameters, let us understand some basic concepts.

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4.1. SOME BASIC CONCEPTS

Some of the important terms which are frequently used in the study of thermodynamics are described as follows :

1. System and Surroundings. From thermodynamic point of view the *Universe* can be divided into two parts namely ; *system* and *surroundings.*

System may be defined as *the part of the Universe selected for the purpose of experimental or theoretical investigations*. For example, if we want to study the effect of temperature on the properties of water then water shall constitute the system. A system is said to be *homogeneous* ; if it contains one phase only and on the other hand, it is *heterogeneous* ; if it consists of more than one phases.

Surroundings may be defined as *the part of the Universe other than the system*. For practical purposes, the region in the vicinity of the system under investigation constitutes the surroundings.

The system and surroundings are separated by the real or imaginary boundaries.

2. Types of the System. Systems can be classified into three types :

(*a*) *Open system* (*b*) *Closed system* (*c*) *Isolated system.*

(*a*) **Open system.** *A system which can exchange mass as well as energy with the surroundings* is called an **open system.** For example, calcination of lime stone in the lime kiln.

$$CaCO_3(s) \xrightarrow{\text{Heat}} CaO(s) + CO_2(g)$$

In this case, heat is supplied to the system while CO_2 gas escapes out into the atmosphere.

(*b*) **Closed system.** *A system that can exchange energy with the surroundings and not mass* is called a **closed system.** For example, if heating of calcium carbonate is done in a sealed bulb, it decomposes into CaO and CO_2 but CO_2 does not escape out.

(*c*) **Isolated system.** *A system which can neither exchange mass nor energy with the surroundings* is called **isolated system.** For example, a reaction carried out in a closed and well insulated vessel like thermos flask constitutes an isolated system.

3. Macroscopic system. *A system containing a large number of chemical species (atoms, ions or molecules)* is called **macroscopic system.**

In fact, the word macroscopic conveys the sense of appreciable quantities. *The properties of the system which arise from the collective behaviour of* large number *of species* are called **macroscopic properties.** These properties are *pressure, temperature, volume, composition, refractive index, surface tension, viscosity, density,* etc. For example, in order to note the temperature of water we do not deal with individual molecules but we consider the molecules in bulk.

4. Extensive and Intensive Properties. The various physical properties of the system may be classified into two types :

(*a*) **Extensive properties.** *The properties of the system which depend upon the quantity of matter contained in it* are called **extensive properties.** Some common examples of these properties are *mass, volume, energy, heat capacity,* etc.

(*b*) **Intensive properties.** *The properties of the system which are independent of the quantity of matter present in it* are called **intensive properties.** Some common examples *are temperature, pressure, refractive index, viscosity, specific heat, density,* etc.

5. State of the System. State of the system implies the *conditions of existence of a particular system when its macroscopic properties have definite values*. If any of the macroscopic properties of the system

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changes, the system undergoes a change in its state. For example, consider liquid water as the system at 25°C and one atmosphere pressure. All of its macroscopic properties in this state have definite values. Now, if we simply change the temperature from 25°C to 50°C, the other macroscopic properties will change automatically and attain new definite values. So water at 50°C will constitute another state of the water system. *The macroscopic properties* of the system are also called **state variables** or **state functions.** In order to define the state of the system it is not necessary to specify all its macroscopic properties. The important state variables which are needed to define the state of a particular system are *temperature* (T), *pressure* (P), *volume* (V) and *concentration* (n).

6. State Functions. *The thermodynamic parameters which depend only upon the initial and final states of the system and are independent of the manner as to how the change is brought about,* are called **state functions.** The concept of state function can be easily understood from the following analogy. If we consider '*h*' as the height between the top and bottom of the mountain, then '*h*' is independent of the path followed in reaching the top of the mountain. Here, the parameter *h* is analogous to state function. In thermodynamics, some common state functions are *internal energy* (E), *enthalpy* (H), *entropy* (S), *free energy* (G), *pressure* (P), *temperature* (T), *volume* (V), etc. It may be noted that two very important thermodynamic parameters namely ; *heat* (q) and *work* (w) are not the state functions because they are *path dependent*.

7. Thermodynamic Process. *The operation which brings about the changes in the state of the system* is termed as **thermodynamic process.** A thermodynamic process may be further classified into different types depending upon the conditions under which the changes are brought about. These are :

(*a*) **Isothermal process.** It is a process which is carried out at *constant temperature* ($\Delta T = 0$).

(*b*) **Adiabatic process.** It is a process in which *no heat exchange* occurs between the system and the surroundings ($\delta q = 0$).

(*c*) **Isobaric process.** It is a process which is carried out at *constant pressure* ($\Delta P = 0$).

(*d*) **Isochoric process.** It is a process which is carried out at constant volume ($\Delta V = 0$).

8. Cyclic Process. *It is a process in which the system returns to the original state after undergoing series of changes.* For example in a process shown below the system returns to the original state **A** after successive changes.

$$A\ (P_1V_1T_1) \longrightarrow B\ (P_2V_2T_1) \longrightarrow C\ (P_2V_3T_2) \longrightarrow A\ (P_1V_1T_1)$$

It may be noted that values of internal energy change (ΔE) and enthalpy change (ΔH) for cyclic process is zero.

9. Reversible and Irreversible process. In fact the terms *reversible* and *irreversible* refer to the path or manner in which the process is carried out.

(*a*) **Reversible Process.** *It is a process which is carried out infinitesimally slowly in such a manner that the system remains almost in a state of equilibrium at every state.* The process is conducted in infinite number of steps and the opposing force is only infinitesimally smaller than the direct force.

In such a process the various changes taking place in the direct process can be exactly reversed. This implies that the system can be brought back to initial state without leaving any effect on the surroundings.

For example, consider a gas enclosed in a vessel fitted with a piston. The internal pressure of the gas is balanced by placing some sand on the piston. Now, if we remove a speck of the sand, the external pressure will become infinitesimally smaller than the internal pressure. Thus, the piston moves out and restores the equilibrium conditions. Now, if we go on removing the specks of the sand one after the other, we can ultimately achieve the finite expansion of the gas. The above process of expansion has been carried out in large number of stages and almost under equilibrium conditions and is, therefore, very close to the reversible process. In fact, the reversible processes take infinite time to complete. Hence, the reversible processes are ideal processes and cannot be realised in actual practice.

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(*b*) **Irreversible Process.** A process which does not meet the above requirements is called **irreversible process.** Such a process, in fact, is carried out rapidly and it cannot be reverted without the help of external agency. In fact, all the natural processes are irreversible processes.

FIRST LAW OF THERMODYNAMICS

The first law of thermodynamics deals with the equivalence of various forms of energy and is known as *law of conservation of energy.* Before we take up the development of the mathematical statement of the first law let us understand the concept of *internal energy, work* and *heat.*

4.2. INTERNAL ENERGY (E) AND INTERNAL ENERGY CHANGE (ΔE)

Every substance is associated with a definite amount of energy which depends upon its chemical nature and its state of existence. This energy is called **internal energy (E)** or **intrinsic energy** of the substance. Internal energy of the system, is the energy possessed by all its constituent molecules. The various forms of energies which contribute towards the energy of the molecule are *translational energy* (E_t), *rotational energy* (E_r), *vibrational energy* (E_v), *electronic energy* (E_e), *nuclear energies of constituent atoms* (E_n) and *potential energy due to interaction with neighbouring molecules* (E_{PE}). Internal energy is a **state property** *i.e.*, its value depends only upon the state of the substance but does not depend upon how that state is achieved. For example, CO_2 can be obtained by various methods such as by heating calcium carbonate or by burning coal. However, one mole of CO_2 at N.T.P. is associated with a definite amount of internal energy which does not depend upon the source from which it is obtained. In the similar way, the different substances possess different internal energies even at the same conditions of temperature and pressure.

It may be noted that the *absolute value of internal energy of a substance* cannot be determined because it is not possible to determine the exact values of the constituent energies such as translation, vibrational, rotational energy, etc. However, we can determine change in internal energy (ΔE) which occurs during chemical reactions. It is the difference between the internal energies of the products and that of the reactants, *i.e.*,

$$\Delta E = \Sigma E_{products} - \Sigma E_{reactants}.$$

4.3. CONCEPT OF WORK AND HEAT

Work and heat are two important modes by which the internal energy of the system can be changed.

Work (W). Work is said to be done if the point of application of force undergoes displacement in the direction of force.

Sign conventions. The latest sign conventions regarding work as per recomendations of IUPAC are :

Work done by the system is **negative.**

Work done on the system is **positive.**

The *positive value of* W signifies that the work has been done on the system by the surroundings and it has contributed to an *increase in the internal energy of the system.* On the other hand, negative value of W indicates that work has been done by the system *(or negative work has been done on the system)* and it has contributed to a *decrease in the internal energy of the system.*

Units of work. In *CGS* units, the work is expressed in *ergs* but in *SI* units, work is expressed in *Joules.* The equivalence between Joules and other units of work is

$$1\ J = 10^7\ ergs = 1\ Nm = 1\ kgm^2\ s^{-2}.$$

The common forms of work that we come across in the study of the thermodynamics are :

(*a*) *Pressure volume work* and (*b*) *Electrical work.*

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(*a*) **Pressure volume work.** This type of work is significant in systems which consist of gases and involve changes in volume against the external pressure.

Expression for PV-work. In order to derive the expression for the pressure-volume (PV) work let us consider a gas enclosed in a cylinder fitted with a frictionless piston having area of cross- section equal to '*a*'. Let the gas expand against the external pressure P forcing the piston to move through a small distance *l*. Now, work of expansion is given by

$$W = \text{Force} \times \text{displacement}$$
$$= F \times l$$

F, the force responsible for moving the piston is given by the product of *pressure* and *area i.e.*,

$$F = P \times a$$
$$\therefore \quad W = P \times al$$

Since *al* refers to the change in volume (ΔV), *i.e.*, $(V_2 - V_1)$, therefore, work done is given by

$$W = P\Delta V$$

During expansion, the work is done by the system and $\Delta V\ (V_2 - V_1)$, *is positive*. Therefore, in order to satisfy the sign conventions, a negative sign is put in the expression for work

$$W = -P\Delta V$$

It may be noted that above expression of work also holds good even for compression process in which the work is done on the system. $\Delta V\ (V_2 - V_1)$, for compression is *negative*. Therefore, work as obtained from the above expression comes out to be *positive* and satisfies the conventions.

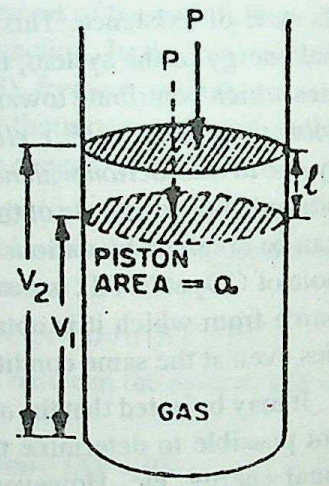

Fig. 4.1

Following the above discussion, *the general expression for all type* of **PV-work** *can be written as* :

$$\boxed{W = -P\Delta V} \quad ...(4.1)$$

Work done in Isothermal Reversible Expansion of Ideal Gas

In order to derive the expression in isothermal reversible expansion of an ideal gas let us consider *n* moles of ideal gas enclosed in a cylinder fitted with a weightless and frictionless piston. The work of expansion for a small change of volume *d*V against the external pressure P is given by the expression

$$\delta w = -PdV \quad ...(i)$$

For ideal gas, $PV = nRT$

$$\therefore \quad P = \frac{nRT}{V}$$

Thus, $$\delta w = -nRT\frac{dV}{V} \quad ...(ii)$$

The work done for finite change of volume $\Delta V\ (V_2 - V_1)$, can be obtained by integration of expression (*ii*) between the limit V_1 to V_2

$$W = \int_{V_1}^{V_2} -nRT\frac{dV}{V}$$

$$= -nRT \ln\frac{V_2}{V_1} = -2.303\ nRT \log\frac{V_2}{V_1} = -2.303\ nRT \log\frac{P_1}{P_2}$$

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(*b*) **Electrical work.** This type of work is significant in electrochemical cells, where redox reaction occurs and the charge is transferred through the external circuit. If Q is the charge flowing through the conductor and E is the potential difference across the conductor, then electrical work is given by the expression

$$W_{Elec} = EQ.$$

Electrical is also known as *non-PV-work* or *non-expansion work.*

Heat (q). Heat is another mode of changing the internal energy of the system. If heat is absorbed by the system, its internal energy increases whereas if heat is given out by the system, its internal energy decreases. This mode of exchange of energy between system and surroundings is possible only if temperature difference exists between them.

Sign conventions. According to international conventions,

Heat absorbed by the system is **positive,**

Heat given out by the system is **negative.**

Difference between heat and work. Let us compare the effect of addition of heat work on a gaseous system.

(*i*) When *heat is added* to a gas, its molecules move faster in all the directions at random. Thus, **heat** *can be regarded as a mode which stimulates the random motion.*

(*ii*) When a piston compresses the gas in order to *do work on it,* the initial effect is to force the molecules in the direction of the piston's movement. Thus, **work** *may be regarded as mode that stimulates the organised motion.*

In simple words ***heat** refers to random form of energy whereas **work** refers to organised form of energy.*

Statement of First Law of Thermodynamics

The first law of thermodynamics is also called the **law of conservation of energy** and governs the transference of energy between the system and the surroundings. The law was first of all stated by *Mayer* and *Halmholtz* (1840) and is purely based upon the human experience that the ***generation of any kind of energy is impossible without the expenditure of an equivalent amount of another kind of energy.*** The law can also be stated in a number of ways as :

In any physical or chemical process, the energy of system and surroundings taken together remains constant

Or

Energy of the universe is always conserved.

Justification of first law of thermodynamics. Although there is no direct proof in favour of first law of thermodynamics, yet the validity of this law is justified by the following points :

(*i*) It has not been possible to construct a *prepetual motion machine, i.e.,* a machine that can do work without consuming energy.

(*ii*) Energy is conserved in chemical reactions also. For example, during electrolysis of water 286 kJ mol^{-1} of energy is consumed. The same amount of energy is released when hydrogen and oxygen combine to form one mole of water.

$$H_2O(l) + 286\ kJ \longrightarrow H_2(g) + \frac{1}{2}O_2(g)$$

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l) + 286\ kJ$$

(*iii*) **James Joules** (1850) conducted many experiments on interconversion of heat and work. He found that for every 4.183 joules of work done one calorie of heat is produced. This exact equivalence of mechanical work and heat is independent of the manner in which the change is brought about and thus, justifies the first law of thermodynamics.

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Mathematical Expression of First Law

In order to arrive at the mathematical statement of the first law of thermodynamics let us consider a system whose internal energy is E_1.

Let the system be supplied q amount of heat, then the internal energy of the system will be raised to $E_1 + q$. Now, if w amount of work is done on the system, then the final internal energy E_2 of the system will be given by

$$E_2 = E_1 + q + w$$

or

$$(E_2 - E_1) = q + w$$

or

$$\Delta E = q + w \quad ...(4.2)$$

w, here includes all types of work, *i.e., pressure-volume* work as well as *non-expansion work.* The relationship (4.2) constitutes mathematical statement of first law of thermodynamics.

For a system which involves only *pressure-volume work,* $w = -P\Delta V$. Therefore, in such a case, the expression (4.2) can be written as

$$\Delta E = q - P\Delta V \quad ...(4.3)$$

It may be noted that q and w are not *the state functions but the sum of the two i.e.,* q + w *which represents* ΔE *is a state function.* Let us prove it with the help of an example. Consider a system which is brought from initial state to final state by following two paths as described below.

Path I. *10 kJ of heat is absorbed by the system and 4 kJ of work is done by it.*

Here,

$$q = 10 \text{ kJ}$$

$$w = -4 \text{ kJ}$$

$$\Delta E = q + w = 10 - 4 = \mathbf{6\ kJ.}$$

Path II. *8 kJ of work is done on the system and 2 kJ of heat is given out by it.*

Here,

$$q = -2 \text{ kJ}$$

$$w = +8 \text{ kJ}$$

$$\Delta E = q + w = -2 + 8 = \mathbf{6\ kJ.}$$

Thus, we find that although values of q and w in two paths are different, yet the value of ΔE is same and is independent of path.

Example 4.1. *A sample of gas is compressed by an average pressure of 0.50 atmosphere so as to decrease its volume from 400 cm^3 to 200 cm^3. During the process 8.00 J of heat flows out to surroundings. Calculate the change in internal energy of the system.*

Solution. Here, $\Delta V = 200 - 400 = -200 \text{ cm}^3 = -0.2 \text{ L}$

External pressure (P) $= 0.50$ atm

$$w = -P\Delta V = -0.50 \times (-0.2) = 0.1 \text{ L-atm.}$$

Now $1 \text{ L-atm} = 101.3 \text{ J}$

$$w = 0.1 \times 101.3 = 10.13 \text{ J}$$

$$q = -8.00 \text{ J}$$

$$\Delta E = q + w = -8.00 + 10.13 \text{ J} = \mathbf{2.13\ J.}$$

Example 4.2. *A gas cylinder of 10 L capacity containing 4 kg of He gas at 27°C developed leakage leading to the escape of the gas into atmosphere. If atmospheric pressure is 1.0 atm. Calculate the work done by the gas assuming ideal behaviour.*

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Solution. Number of moles of gas $n = \frac{4 \times 10^3}{4} = 10^3$ moles

Initial volume, $V_1 = 5\ L\ ;\ T = 27 + 273 = 300\ K$

Final volume $V_2 = \frac{nRT}{P} = \frac{10^3 \times 0.0821 \times 300}{1} = 24630\ L$

$$\Delta V = V_2 - V_1 = 24630 - 5 = 24625\ L$$

$$W_{PV} = -P\Delta V = -1 \times 24625\ L\text{-atm}$$

$$= -24625 \times 101.3\ J$$

$$= -24625 \times 101.3 \times 10^{-3}\ kJ.$$

$$= \mathbf{-2.494 \times 10^3\ kJ.}$$

REVIEW PROBLEMS

4.1. A sample of gas expands from 500 cm^3 to 700 cm^3 against the average pressure of 750 mm. At the same time 2 J of heat flows into the system. Calculate the change in internal energy.

4.2. A system has internal energy E_1. If 600 J of heat is supplied to it and at the same time it does 450 J of work. Calculate the value of E_2, *i.e.*, internal energy in the new state.

4.3. Calculate the change in internal energy when the system absorbs 400 J of heat and does 240 J of work on surroundings.

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Significance of ΔE

The significance of ΔE directly follows from the first law of thermodynamics, according to which

$$\Delta E = q + w$$

Now if we assume that only pressure-volume work is done during the change then the expression becomes

$$\Delta E = q - P\Delta V \qquad (\because\ w = -P\Delta V)$$

If the process is carried out at constant volume, then

$$\Delta V = 0$$

Therefore, under these conditions

$$\Delta E = q_{(v)} \qquad ...(4.4)$$

Thus, ΔE represents the heat change taking place when the process occurs at constant volume and constant temperature.

Experimental Determination of Internal Energy Change (ΔE)

The heat changes in reactions can be measured with the help of **calorimeters.** There are different types of calorimeters depending upon the requirements of a particular experiment. In general, reactions taking place at constant volume and involving gases are carried out in a closed container with rigid walls which could withstand high pressures developed. One such vessel is a **bomb calorimeter**. It is made of heavy steel. The steel vessel is coated inside with gold or platinum to avoid oxidation of steel during the chemical reactions. The vessel is fitted with a tight screw cap. There are two electrodes R_1 and R_2 which are connected to each other through a platinum wire S as shown in Fig. 4.2.

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The wire S remains dipping in a platinum cup just below it.

A small amount of the substance under investigation is taken in platinum cup. The vessel is then filled with excess of oxygen at a pressure of about 20 to 25 atmospheres and is subsequently sealed. It is now dipped in a insulated water bath which is also provided with a mechanical stirrer and a thermometer, sensitive enough to read upto 0.01°C (Beckmann's thermometer).

The initial temperature of water is noted and combustion is initiated by passing electric current through the platinum wire. The heat evolved during the chemical reactions raises the temperature of water which is recorded from the thermometer. By knowing the heat capacity of calorimeter and also the rise in temperature, the heat of combustion at constant volume can be calculated by using the expression.

$$\Delta E = Z \times \Delta T \times \frac{M}{w}$$

where, Z = Heat capacity of calorimeter system

ΔT = Rise in temperature

M = Molecular mass of substance

w = Mass of substance taken.

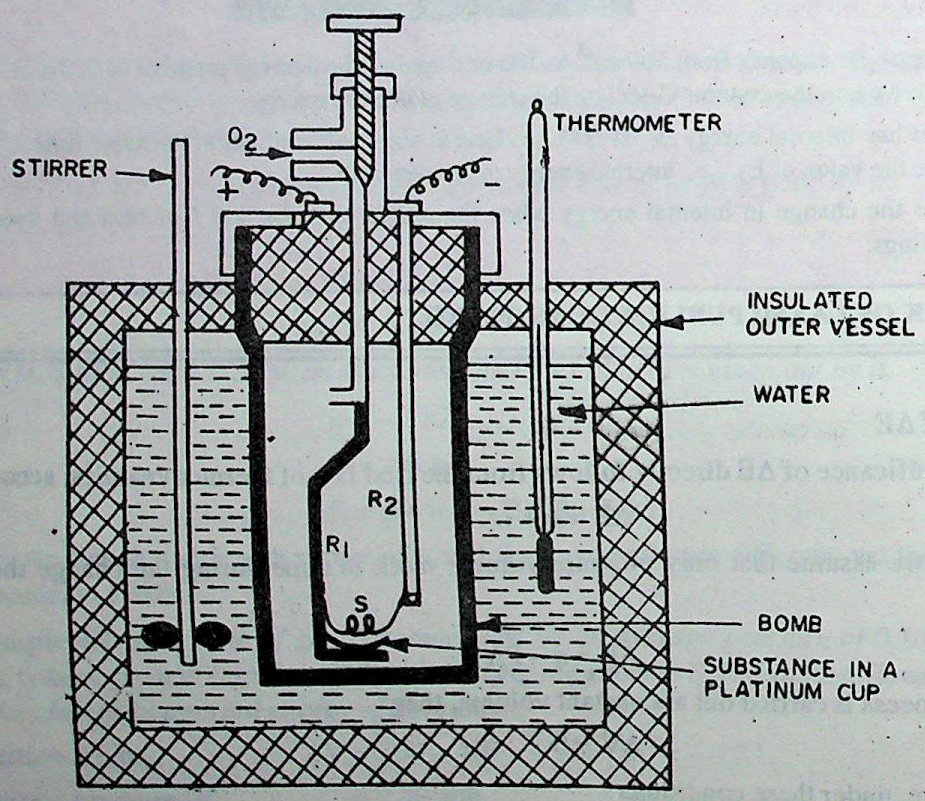

Fig. 4.2. Bomb calorimeter.

4.4. ENTHALPY (H) AND ENTHALPY CHANGE (ΔH)

It has already been pointed out that heat change during the reaction at *constant temperature* and *constant volume* is given by internal energy change (ΔE).

However, most of the reactions in the laboratory are carried out in open beakers or test tubes, etc. In such cases, the reacting system is open to atmosphere. Since atmospheric pressure is almost constant, therefore, such reactions may involve the change in volume against the constant atmospheric pressure. The heat changes occurring during such reactions may not be equal to the internal energy change. In order to understand this,

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let us assume a chemical reaction involving gaseous substances, which proceeds with the evolution of heat. When the reaction is carried out at constant pressure two possibilities arise :

(*a*) If the reaction proceeds with the increase in volume the system has to expand against the atmospheric pressure and energy is required for this purpose. The heat evolved in this case would be little less than the heat evolved at constant volume, because a part of the energy has to be utilised for expansion.

(*b*) If the reaction proceeds with contraction of volume at constant pressure, the work is done on the system and heat evolved will be greater than the heat evolved at constant volume.

Thus, we conclude that the heat changes occurring at *constant pressure* and *constant temperature* are not merely due to the changes in internal energy alone but also include energy changes due to expansion or contraction against the atmospheric pressure. In order to study the heat changes of chemical reactions at constant temperature and constant pressure a new term *enthalpy* is introduced.

Enthalpy may defined as the *sum of the internal energy and the pressure volume energy of the system under a particular set of conditions*. It is denoted by **H** and is mathematically expressed by the following relation :

$$H = E + PV$$

where **H** is enthalpy, **E** is internal energy, **P** is pressure and **V** is volume.

It may be noted that like internal energy (**E**), enthalpy (**H**) is also a **state function**. The absolute value of enthalpy cannot be determined, however the change in enthalpy (**ΔH**) can be experimentally determined. In chemical processes, the change in enthalpy can be expressed as

$$\Delta H = H_P - H_R$$

where, H_P is enthalpy of the products ; and

H_R is enthalpy of the reactants.

Significance of ΔH

The significance of **ΔH** can be understood by considering an isothermal process occurring at constant pressure. According to first law of thermodynamics, the net heat absorbed (**q**) is related to the internal energy change (**ΔE**) and work done (**W**) by the mathematical expression

$$\Delta E = q + w$$

or

$$q = \Delta E - w$$

If the work done during the change is only *PV work*, then

$$q = \Delta E - (-P\Delta V)$$

or

$$q = \Delta E + P\Delta V \qquad ...(4.5)$$

Also by definition, the enthalpy **H** is given by

$$H = E + PV$$

The change in enthalpy **ΔH** is given by

$$\Delta H = \Delta E + \Delta(PV)$$

$$= \Delta E + P\Delta V + V\Delta P$$

Pressure P is kept constant, $\Delta P = 0$

$$\Delta H = \Delta E + P\Delta V \qquad ...(4.6)$$

From equations (4.5) and (4.6), we can deduce that

$$\Delta H = q_{(P)} \qquad ...(4.7)$$

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Therefore, the enthalpy change represents the heat change taking place during the process occurring at constant temperature and constant pressure.

Experimental Determination of Enthalpy Change (ΔH)

The change in enthalpy of a reaction is also measured in a calorimeter. However, the calorimeter used is kept upon to the atmosphere. The calorimeter is immersed in an insulated water bath fitted with stirrer and thermometer. The temperature of the bath is recorded in the beginning and after the end of the reaction and the change in temperature is calculated. Knowing the heat capacity of water bath and calorimeter and also the change in temperature, the heat absorbed or evolved in the reaction can be calculated. This gives the enthalpy change (ΔH) of the reaction.

Relationship Between ΔH and ΔE

In order to derive the relationship between ΔH and ΔE, let us consider a reaction involving gases. Let the process be isothermal and carried out at constant pressure (P). If V_A be the total volume of the gaseous reactants and V_B be the total volume of the gaseous products, also n_A be the number of moles of gaseous reactants and n_B be the number of moles of gaseous products. Then

$$PV_A = n_A RT$$

and

$$PV_B = n_B RT$$

$$PV_B - PV_A = (n_B - n_A)RT$$

or

$$P(V_B - V_A) = (n_B - n_A)RT$$

or

$$P\Delta V = (\Delta n)RT$$

The change in enthalpy during the process at constant pressure is given by the expression

$$\Delta H = \Delta E + P\Delta V$$

Substituting the value of PΔV, we have

$$\Delta H = \Delta E + (\Delta n)RT \quad ...(4.8)$$

Δn, here, refers to the change in the number of moles of *gaseous species* during the process. The difference between ΔH and ΔE will depend upon the magnitude as well as sign of **Δn**. For example,

if Δn is 0 ; $\Delta H = \Delta E$

if Δn is – ve ; $\Delta H < \Delta E$ and

if Δn is + ve ; $\Delta H > \Delta E$.

From equations (4.4) and (4.7) substitute the values of ΔH and ΔE in equation (4.8).

$$q_{(P)} = q_{(v)} + (\Delta n)RT \quad ...(4.9)$$

In short,

$\Delta H = \Delta E + P\Delta V$	or	$\Delta H = \Delta E + \Delta n_g RT$
$q_{(P)} = q_{(V)} + P\Delta V$	or	$q_{(P)} = q_{(V)} + \Delta n_g RT$

Notes : (*i*) *For chemicals reactions involving no change in volume or those having same number of gas moles in reactants and products or those involving no gaseous reactant or products.*

$$q_{(P)} = q_{(V)} \quad \text{or} \quad \Delta H = \Delta E$$

(*ii*) *While solving numerical problems using equation (4.8) or (4.9), R must be taken equal to 0.002 k Cal K^{-1} mol^{-1} if ΔH, ΔE values are given in k Cal and it is taken equal to 8.31 JK^{-1} mol^{-1} if ΔH, ΔE values are given joules.*

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Example 4.3. *The heat of combustion of napthalene ($C_{10}H_8(s)$) at constant volume was measured to be – 5133 kJ mol^{-1} at 298 K. Calculate the value of enthalpy change ($R = 8.314\ JK^{-1}\ mol^{-1}$).*

Solution. The combustion equation of naphthalene is

$$C_{10}H_8(s) + 12O_2(g) \longrightarrow 10CO_2(g) + 4H_2O(l)\ ;\ \Delta E = -5133\ \text{kJ}$$

$$\Delta n = 10 - 12 = -2\ \text{mol}$$

Now, applying the relation,

$$\Delta H = \Delta E + (\Delta n)RT$$

$$= -5133 \times 10^3\ \text{J} + (-2\ \text{mol})\ (8.314\ \text{J mol}^{-1}\ \text{K}^{-1})\ (298\ \text{K})$$

$$= -5133000\ \text{J} - 4955.14\ \text{J} = \mathbf{-5128044.9\ J.}$$

Example 4.4. *For a gaseous reaction*

$$2A_2(g) + 5B_2(g) \longrightarrow 2A_2B_5(g)$$

at 27°C the heat change at constant pressure is found to be – 50160 J. Calculate the value of internal energy change (ΔE). Given that $R = 8.314\ JK^{-1}\ mol^{-1}$.

Solution. The given chemical reaction is

$$2A_2(g) + 5B_2(g) \longrightarrow 2A_2B_5(g)\ ;\ \Delta H = -50160\ \text{J}$$

$$\Delta n = 2 - (5 + 2) = -5\ \text{mol}$$

Now applying the relation,

$$\Delta H = \Delta E + (\Delta n)\ RT$$

$$-50160\ \text{J} = \Delta E + (\Delta n)\ RT$$

$$\Delta E = -50160\ \text{J} - \Delta nRT$$

$$= -50160\ \text{J} - (-5\ \text{mol})\ (8.314\ \text{JK}^{-1}\ \text{mol}^{-1})\ (300\ \text{K})$$

$$= -50160\ \text{J} + 12471\ \text{J} = \mathbf{-37689\ J.}$$

REVIEW PROBLEMS

4.4. The heat of combustion of methane at constant volume is measured in a bomb calorimeter at 298 K and is found to be – 885 kJ mol^{-1}. Calculate the heat of combustion at constant pressure.

4.5. The heat produced by combustion of 1.0 g of benzene (C_6H_6) at constant volume is 41.80 kJ at 298 K. Calculate the value of enthalpy of combustion of benzene at 298 K.

4.6. If ΔE for the process : $MgCO_3(s) \longrightarrow MgO(s) + CO_2(g)$ is 111.4 kJ at 402 K and 1 atm pressure calculate the value of ΔH.

4.7. Calculate ΔH of the reaction. Given that at 298 K

$$NH_4Cl(aq) + NaNO_2(s) \longrightarrow NaCl(s) + 2H_2O(l) + N_2(g)\ ;\ \Delta E = -332\ \text{kJ}.$$

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Enthalpy of Reaction. *It is the enthalpy change taking place during the reaction when the number of moles of reactants and products are same as the stoichiometric coefficients indicated in the balanced chemical equation.* Since most of the reactions are carried out at constant temperature and constant pressure, the enthalpy

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of reaction is also called **heat of reaction.** The enthalpy change of the reaction depends upon the conditions like temperature, pressure, etc., under which the chemical reaction is carried out. Therefore, it is necessary to select the *standard* or *reference state* conditions. According to thermodynamic conventions, the **standard state** refers to **1 atmosphere pressure** and **298 K temperature.** *The enthalpy change of a reaction at the standard state conditions* is called **standard enthalpy of the reaction.** It is denoted by $\Delta H°$.

Standard Enthalpy of Formation ($\Delta H_f°$). ***The standard enthalpy of formation, is defined as the enthalpy change taking place during the formation of one mole of substance from its constituent elements, all the substances being in their standard states.*** For example, the value of $\Delta H_f°$ of $H_2O(l)$ is -286 kJ mol^{-1}. It refers to the enthalpy change of the following reaction in standard state.

$$H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)\ ;\ \Delta H = -286.0 \text{ kJ}$$

It may be noted that :

(*i*) *The standard enthalpy of formation of the substance is also called its* **standard enthalpy** *and can also be denoted by* **H°**.

(*ii*) *The standard state of the element is pure element in its most stable form at 298 K and one atmosphere pressure.* For example, standard state of *carbon, oxygen, sulphur, mercury, bromine* and *iodine* are C (*graphite*), $O_2(g)$, S (*rhombic*), $Br_2(l)$ and $I_2(s)$ respectively.

(*iii*) *Since absolute value of enthalpy cannot be known, therefore, the standard enthalpy (i.e. the standard enthalpy of formation) of free elements are taken to be* **zero** *by convention.*

The standard enthalpies of various elements and compounds are given in Table 4.1.

Table 4.1. Standard Enthalpies of Formation at 298 K

Substance	$\Delta H_f°$ (298) (kJ mol^{-1})	*Substance*	$\Delta H_f°$ (298) (kJ mol^{-1})
$H_2(g)$	0.0	$Br_2(l)$	0.0
$H(g)$	217.7	$Br_2(g)$	30.71
$H_2O(l)$	– 286.0	$I_2(s)$	0.0
$H_2O(g)$	– 241.8	$I_2(g)$	62.26
$H_2O_2(l)$	– 188.0	$Cl(g)$	121.4
$C(g)$	– 718.4	$Br(g)$	111.8
C (*diamond*)	1.896	$I(g)$	106.6
C (*graphite*)	0.0	$HF(g)$	– 268.6
$CO(g)$	– 110.5	$HCl(g)$	– 92.30
$CO_2((g)$	– 393.5	$HBr(g)$	– 36.23
$CH_4(g)$	– 74.85	$HI(g)$	25.44
$C_2H_6(g)$	– 84.68	$H_2S(g)$	– 20.17
$C_2H_4(g)$	52.30	S (*rhombic*)	0.0
$C_2H_2(g)$	226.7	S (*monoclinic*)	0.2971
$C_2H_6(l)$	49.04	$SO_2(g)$	– 296.9
$N_2(g)$	0.0	$CaCO_3$(*calcite*)	– 120.7
$N(g)$	472.7	$Hg(l)$	0.0
$NO(g)$	90.37	$Hg_2Cl_2(s)$	– 264.9
$NO_2(g)$	33.85	$NaCl(s)$	– 411.0

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Substance	ΔH_f° (298) ($kJ\ mol^{-1}$)	Substance	ΔH_f° (298) ($kJ\ mol^{-1}$)
$N_2O(g)$	81.85	$Na_2CO_3(s)$	– 113.1
$NH_3(g)$	– 46.19	$KCl(s)$	– 435.9
$O_2(g)$	0.0	$KNO_3(s)$	– 492.7
$O_3(g)$	142.3	$AgCl(s)$	– 127.0
$O(g)$	247.5	$H_2O(l)$	– 286.0
$F_2(g)$	23.0	$H_2SO_4(l)$	– 814.0

4.5. APPLICATIONS OF FIRST LAW OF THERMODYNAMICS

One of the important outcome of first law of thermodynamics is **Hess's Law**. The law was put forth by *G.H. Hess* and states that

" the enthalpy change in a chemical or physical process is same whether the process is carried out in one step or in several steps."

It implies that when a reaction is carried out in several steps, the overall enthalpy change must be equal to the sum of the enthalpy changes for individual steps. For example, consider a process involving the conversion of reactant A into B in one step along path I. The enthalpy change of a process is represented by ΔH. Now suppose, the same process is carried out in two steps involving a change form A to C and C to B according to path II Fig. 4.3. Let ΔH_1 and ΔH_2 be enthalpy changes from A to C and C to B respectively. Then according to Hess's law :

$$\Delta H = \Delta H_1 + \Delta H_2$$

Hess's law is simply a corollary of the first law of thermodynamics. It implies that enthalpy change of a reaction depends on the initial and final state and is independent of the manner by which the change is brought about. If ΔH were path dependent, it would have been possible to create or destroy energy by taking the system from A $\longrightarrow$ B by path I and from B $\longrightarrow$ A by path II which is against the law of conservation of energy.

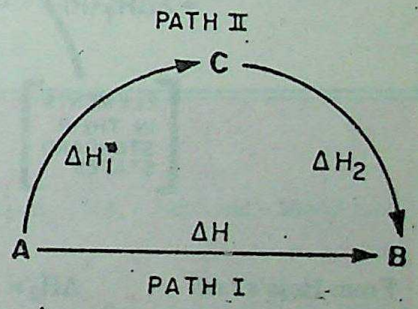

Fig. 4.3. Illustration of Hess's Law.

Applications of Hess's Law

The practical utility of Hess's law lies in the fact that it enables us to calculate the enthalpy changes for the reactions which are experimentally not possible. Their enthalpy change can be calculated from the experimentally determined values of ΔH of some other reactions. The Hess's law cycle is considered in such a way so that the unknown reaction forms one of its segment while the reactions whose ΔH values are known, form the other segments. This is illustrated in the following applications.

1. Determination of enthalpy of formation. There are large number of compounds such as C_6H_6, CO, C_2H_6 etc., whose direct synthesis from their constituent elements is not possible. Their ΔH_f° values can be determined indirectly by Hess's law. For example, let us consider Hess's law cycle for $CO_2(g)$ to calculate the ΔH_f° of $CO(g)$ which cannot be determined otherwise. The Hess's law cycle showing the formation of CO_2 and CO has been diagramatically shown below in Fig. 4.4.

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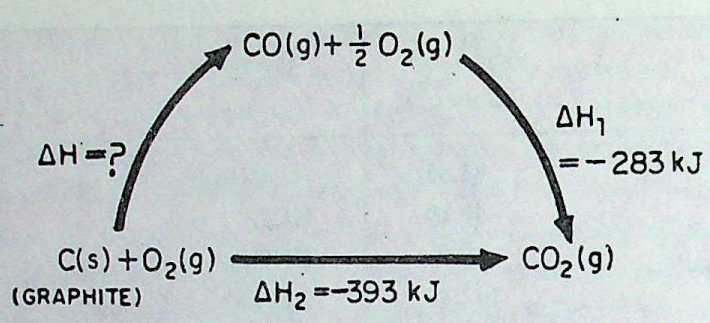

Fig. 4.4

Now, according to Hess's law $\Delta H_2 = \Delta H_1 + \Delta H$

$\therefore \quad \Delta H = \Delta H_2 - \Delta H_1$

The values of ΔH_2 and ΔH_1 can be measured experimentally and have been found to be – 393.5 kJ and – 283.0 kJ respectively.

$\therefore \quad \Delta H = -393.5 - (-283.0) = \mathbf{-110.5\ kJ.}$

2. Calculation of standard enthalpies of reactions. From the knowledge of the standard enthalpies of formation of reactants and products, the standard enthalpy of reaction can be calculated using Hess's law. In general the Hess's law cycle representing the formation of reactants and products from their respective elements in the standard state is considered as shown in Fig. 4.5.

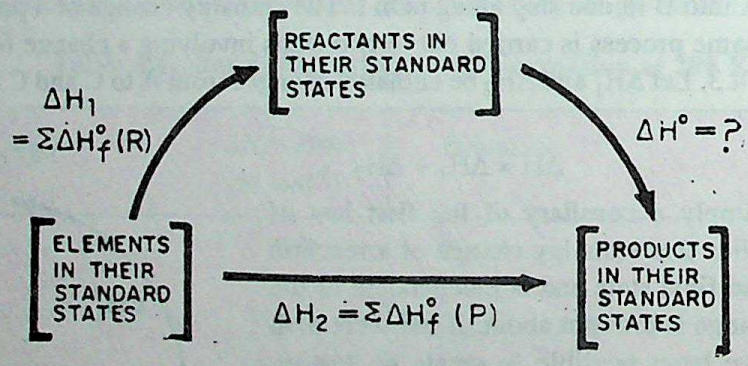

Fig. 4.5

From Hess's law $\quad \Delta H_2 = \Delta H^\circ + \Delta H_1$

or $\quad \Delta H^\circ = \Delta H_2 - \Delta H_1$

$$= \Sigma\Delta H_f^\circ\ (P) - \Sigma\Delta H_f^\circ\ (R)$$

$$= \begin{bmatrix} \textit{Sum of standard} \\ \textit{enthalpies of} \\ \textit{formation of} \\ \textit{products} \end{bmatrix} - \begin{bmatrix} \textit{Sum of standard} \\ \textit{enthalpies of} \\ \textit{formation of} \\ \textit{reactants} \end{bmatrix}$$

For example, consider a hypothetical reaction

$$aA + bB \longrightarrow lL + mM$$

$$\Delta H^\circ = \Sigma\Delta H_f^\circ\ (\textit{products}) - \Sigma\Delta H_f^\circ\ (\textit{reactants})$$

$$= [l\Delta H_f^\circ\ (L) + m\Delta H_f^\circ\ (M)] - [a\Delta H_f^\circ\ (A) + b\Delta H_f^\circ\ (B)].$$

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Example 4.5. *Calculate the standard enthalpy change for a reaction :* $CO_2(g) + H_2(g) \longrightarrow CO(g) + H_2O(g)$ *given that* ΔH_f° *for* $CO_2(g)$, $CO(g)$ *and* $H_2O(g)$ *as* – 393.5, – 110.5 *and* – 241.8 *kJ mol*$^{-1}$ *respectively.*

Solution. ΔH° for the reaction is given as

$$\Delta H^\circ = \Sigma\Delta H_f^\circ\ (products) - \Sigma\Delta H_f^\circ\ (reactants)$$
$$= [\Delta H_f^\circ\ (H_2O) + \Delta H_f^\circ\ (CO)] - [\Delta H_f^\circ\ (CO_2) + \Delta H_f^\circ\ (H_2)]$$

Substituting the given values, we get

$$\Delta H^\circ = [-241.8 - 110.5] - [-393.5 + 0]$$
$$= -352.3 + 393.5 = \mathbf{+41.2\ kJ.}$$

Example 4.6. *Calculate standard enthalpy change* (ΔH°) *and standard internal energy change* (ΔE°) *for the reaction :*

$$OF_2(g) + H_2O(g) \longrightarrow O_2(g) + 2HF(g)$$

Given that standard enthalpies of formation ΔH_f° *of* $OF_2(g)$, $H_2O(g)$ *and* $HF(g)$ *as* + 23.0, – 241.8, 268.6 *kJ mol*$^{-1}$ *respectively.* [A.I. CBSE (O), 1991]

Solution.

$$\Delta H^\circ = \Sigma\Delta H_f^\circ\ (products) - \Sigma\Delta H_f^\circ\ (reactants)$$
$$= 2(-268.6\ kJ) - \{(+23.0\ kJ) + (-241.8\ kJ)\}$$
$$= -537.2\ kJ + 218.8\ kJ = \mathbf{-318.4\ kJ}$$

Calculation of ΔE° $\quad \Delta n = 3 - 2 = +1$ mol

We know that $\quad \Delta H^\circ = \Delta E^\circ + (\Delta n)RT \quad$ (T = 298 K)

$\therefore \quad \Delta E^\circ = \Delta H^\circ - (\Delta n)RT$

$$= -318.4\ kJ - (1\ mol)(8.314\ JK^{-1}\ mol^{-1})(298\ K)$$
$$= -318.4\ kJ - 2476\ J = -318.4\ kJ - 2.477\ kJ$$
$$= \mathbf{-320.877\ kJ.}$$

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4.8. The standard enthalpies of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(l)$ respectively – 74.8, – 393.5 and – 286 kJ mol^{-1}. Calculate the standard enthalpy change for the reaction :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

4.9. Calculate enthalpy of combustion of benzene. Given that the standard enthalpies of formation of $C_6H_6(l)$, $CO_2(g)$, $H_2O(l)$ as – 49.04, – 393.5 and – 286 kJ mol^{-1} respectively.

4.10. Given the standard enthalpies of formation of $CO(g)$ and $H_2O(g)$ as – 110.5 kJ and – 241.8 kJ mol^{-1} respectively. Calculate ΔH° and ΔE° for the reaction :

$$C(s) + H_2O(g) \longrightarrow CO(g) + H_2(g).$$

4.11. Calculate the standard enthalpy of combustion of ethanol. Given that ΔH_f° of $C_2H_5OH(l)$, $CO_2(g)$; $H_2O(l)$ as – 277.7 kJ mol^{-1}, – 393.5 kJ mol^{-1}, – 286 mol^{-1} respectively.

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3. Calculation of bond energies. It is a well known fact that the process of formation of a chemical bond is accompanied by the release of energy. Conversely, the energy has to be supplied for the breaking of a bond. *The energy required to break a particular bond in a gaseous molecule* is referred to as **bond dissociation energy**. It is a definite quantity and is expressed in *kJ mol*$^{-1}$.

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In a **diatomic molecule**, the *bond dissociation* energy is same as *bond energy*. For example, the energy required to break one mol of H—H bonds in gaseous state is 435.4 kJ. Therefore, bond dissociation energy or bond energy of H—H bond is 435.4 kJ mol^{-1}. This may be expressed as :

$$\Delta H_{H-H} = 435.4 \text{ kJ mol}^{-1}$$

However, in a **polyatomic molecule**, the bond dissociation energy is not the same for successive bonds although they may be of the same type. Therefore, in such a case the bond energy is not equal to the bond dissociation energy. For example, in water, H_2O, the bond dissociation energies of the two O—H bonds differ from one another as described below :

$$HO-H(g) \longrightarrow H(g) + OH(g) \; ; \; \Delta H = 498 \text{ kJ}$$

$$O-H(g) \longrightarrow H(g) + O(g) \; ; \; \Delta H = 430 \text{ kJ}.$$

In such a case, therefore, the *bond energy* is expressed as the average of the *bond dissociation energies* of various similar bonds. For example, the bond energy of O—H bond is expressed as

$$\Delta H_{O-H} = \frac{498 + 430}{2} = 464 \text{ kJ mol}^{-1}.$$

Thus, **bond energy** may be defined as the ***average amount of energy required to break one mole bonds of that type in gaseous molecules***. The bond energies of various bonds have been given in Table 4.2.

The bond dissociation energy can be calculated by the use of Hess's law as described below :

For example, bond dissociation energy of HCl is the standard enthalpy change, $\Delta H°$ of the following reaction :

$$HCl(g) \longrightarrow H(g) + Cl(g)$$

$$\Delta H° = \Sigma \Delta H_f° \text{ (products)} - \Sigma \Delta H_f° \text{ (reactants)}$$

Now it is known that $\Delta H_f°$ of

$$HCl(g) = -92.2 \text{ kJ mol}^{-1}$$

$$H(g) = 217.7 \text{ kJ mol}^{-1}$$

$$Cl(g) = 121.0 \text{ kJ mol}^{-1}$$

$$\therefore \quad \Delta H° = 217.7 + 121.0 - (-92.2) = 430.9 \text{ kJ mol}^{-1}$$

Thus, $\Delta H°_{H-Cl} = \mathbf{430.9 \text{ kJ mol}^{-1}}$.

Table 4.2. Bond Energies of Some Bonds

Bond	*Bond energy* (kJ mol^{-1})*	*Bond*	*Average bond energy** (kJ mol^{-1})*
H—H	435.4	C = C	619
H—F	565	C ≡ C	812
H—Cl	431	O—H	463
H—Br	364	N—H	389
H—I	297	C—H	413
F—F	155	C—Cl	328
Cl—Cl	242	C—O	335
Br—Br	190	C = O	707
I—I	149	C—N	293

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Bond	*Bond energy* (kJ mol^{-1})*	*Bond*	*Average bond energy** (kJ mol^{-1})*
O = O	494	C = N	616
N ≡ N	941	C ≡ N	879
		C—Br	275.6
		O—O	138
		N—N	159
		N = N	418
		C—C	347

*These bond energies are the dissociation energies of diatomic molecules that have only one bond, they are, therefore, exact values.

**These bond energies are obtained from molecules that contain more than one bond, therefore, they are average values.

Use of bond energy data. The bond energy data given in Table 4.2 is quite useful in determining the standard enthalpies of the reactions. The chemical reaction involves the cleavage of old bonds in reacting species and formation of new bonds to give product molecules. In general,

$$\begin{bmatrix}\textbf{Enthalpy}\\ \textbf{of reaction}\end{bmatrix} = \begin{bmatrix}\textbf{Sum of bond energies}\\ \textbf{of reactants}\end{bmatrix} - \begin{bmatrix}\textbf{Sum of bond energies}\\ \textbf{of products}\end{bmatrix}$$

Thus, the values given in bond energy data can help us in :

(*i*) Calculating standard enthalpy of reactions.

(*ii*) Calculation of bond energies of some specific bond in the molecule.

Some examples are being discussed as follows :

Example 4.7. *Calculate the enthalpy change (ΔH) of the following reaction*

$2C_2H_2(g) + 5O_2(g) \longrightarrow 4CO_2(g) + 2H_2O(g)$ *given average bond energies of various bonds, i.e., C—H, C ≡ C, O = O, C = O, O—H as 414, 814, 499, 724 and 640 kJ mol^{-1} respectively.*

Solution. The equation representing various substances involved in chemical reaction is :

$$2(H—C \equiv C - H) + 5(O = O) \longrightarrow 4(O = C = O) + 2(H—O—H)$$

The reaction involves the breaking of 4 C—H bonds, 2 C ≡ C bonds, 5 O = O bonds and formation of 8 C = O bonds and 4 O—H bonds.

$$\Delta H = \begin{bmatrix}\text{Total energy required}\\ \text{to break the bonds}\end{bmatrix} - \begin{bmatrix}\text{Energy given out in}\\ \text{forming the bonds}\end{bmatrix}$$

$$= [4\,\Delta H_{C—H} + 2\,\Delta_{C \equiv C} + 5\,\Delta H_{O=O}] - [8\,\Delta H_{C=O} + 4\,\Delta H_{O—H}]$$

$$= (4 \times 414 + 2 \times 810 + 5 \times 499) - (8 \times 724 + 4 \times 460)$$

$$= 5771 - 7632 = \mathbf{-1861\ kJ.}$$

Example 4.8. *Calculate the bond energy of Cl—Cl bond from the following data :*

$CH_4(g) + Cl_2(g) \longrightarrow CH_3Cl(g) + HCl(g)$; $\Delta H = -100.3$ *kJ. Also the bond energies of C—H, C—Cl, H—Cl bonds are 413, 326 and 431 kJ mol^{-1} respectively.*

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Solution. The given reaction is

$$CH_4(g) + Cl—Cl(g) \longrightarrow CH_3—Cl(g) + HCl(g) \; ; \; \Delta H = -100.3 \text{ kJ}$$

As is evident from the equation, the reaction involves the cleavage of one C—H bond, one Cl—Cl bond and formation of one C—Cl bond and one H—Cl bond.

$$\Delta H = [\text{Total energy required}] - [\text{Total energy released}]$$

$$-100.3 = [\Delta H_{C—H} + \Delta H_{Cl—Cl}] - [\Delta H_{C—Cl} + \Delta H_{HCl}]$$

$$= 413 + x - 326 - 431 = x - 344$$

or $$x = 344 - 100.3 = \mathbf{243.7 \text{ kJ mol}^{-1}}.$$

Example 4.9. *Calculate the bond energy of C—H bond in methane from the following data :*

(*a*) $C(s) + 2H_2(g) \longrightarrow CH_4(g)$; $\Delta H = -74.8$ *kJ*

(*b*) $H_2(g) \longrightarrow 2H(g)$; $\Delta H = 435.4$ *kJ*

(*c*) $C(s) \longrightarrow C(g)$; $\Delta H = 718.4$ *kJ*.

Solution. In order to calculate the bond energy of C—H bond let us consider the reaction

$$CH_4(g) \longrightarrow C(g) + 4H(g) \; ; \; \Delta H = ?$$

From Eq. (*a*) ; ΔH_f of $CH_4(g)$ $= -74.8 \text{ kJ mol}^{-1}$

From Eq. (*b*) ; ΔH_f of $H(g)$ $= \dfrac{435.4}{2} = 217.7 \text{ kJ mol}^{-1}$

From Eq. (*c*) ; ΔH_f of $C(g)$ $= 718.4 \text{ kJ mol}^{-1}$

Now, ΔH of reaction under consideration is given as

$$\Delta H = \Sigma\Delta H_f(\text{products}) - \Sigma\Delta H_f(\text{reactants})$$

$$= (4 \times 217.7 + 718.4) - (-74.8) = 1664.0 \text{ kJ}$$

$$\Delta H_{C—H} = \frac{\text{Total energy required}}{\text{No. of C—H broken}}$$

$$= \frac{1664.0}{4} = \mathbf{416.0 \text{ kJ mol}^{-1}}.$$

REVIEW PROBLEMS

4.12. Calculate the bond energy of HBr bond. Given that enthalpy of formation of HBr is $-36.2 \text{ kJ mol}^{-1}$. The bond energies of H—H and Br—Br bonds are 431 kJ and 188 kJ mol^{-1} respectively.

4.13. Calculate the enthalpy of hydrogenation C_2H_4 ;

$$C_2H_4(g) + H_2(g) \longrightarrow C_2H_6(g)$$

given the bond energies of H—H, C = C, C—C, C—H bonds as 433, 615, 347 and 413 kJ mol^{-1}.

4.14. Given that enthalpy of formation of $NH_3(g)$, $H(g)$, $N(g)$ as -46, 218, 470.65 kJ mol^{-1} respectively. Calculate the enthalpy of N—H bond.

4.15. Calculate ΔH_f of ethane (C_2H_6) at 25°C. Given that heat of sublimation of graphite is 715 kJ mol^{-1}. Bond energies of H—H, C—H and C—C bonds are respectively 435.4, 413 and 347 kJ mol^{-1}.

4.16. Calculate bond energy of C = C in propene. Given that ΔH_f of propene is $-87.78 \text{ kJ mol}^{-1}$. Bond energies of C—C, C—H and H—H bonds are 347, 413, 435.4 kJ mol^{-1} respectively. Also $C(s) \longrightarrow C(g)$; $\Delta H = 715$ kJ.

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SECOND LAW OF THERMODYNAMICS

The need of second law. First law of Thermodynamics summarizes our experience regarding the interconversion of various forms of energies into one another. However, the **limitation of first law** lies in the fact that it is unable to predict the *feasibility of the change* or *the direction of the change.* For example :

(*a*) If two bodies A and B (capable of exchanging heat) are brought in contact with each other, the first law will fail to predict whether heat will be lost by A or by B. It will simply tell us that if one of them loses some amount of heat, the other will simultaneously gain same amount of heat and *vice versa.* In order to predict the direction of flow of heat we require another parameter *i.e., temperature* of A and B.

(*b*) Similarly, consider a chemical change

$$PCl_5 \rightleftharpoons PCl_3 + Cl_2 \; ; \; \Delta H = -x \text{ kJ}$$

The first law tells us only that if decomposition of one mole of PCl_5 occurs, x, kJ of energy is produced and conversely the combination of PCl_3 and Cl_2 to give one mole of PCl_5 requires x kJ of energy. Now if we have a mixture of PCl_5, PCl_3 and Cl_2, we cannot know from the first law alone whether the reaction would involve dissociation of PCl_5 or the combination of PCl_3 and Cl_2.

The above examples show the insufficiency of the first law of thermodynamics. In order to ascertain the direction of a chemical or physical process we need the knowledge of some other criteria beyond first law. The criteria is provided by Second Law of Thermodynamics. Before we study the statement of second law of thermodynamics let us be familiar with some important terms.

4.6. SPONTANEOUS PROCESSES

In our daily life, we come across many natural processes which take place of their own in one direction but not in the other. For example, water flow down the hill without the help of external agency but water cannot flow up the hill of its own. It can be made to flow upward only by the use of some external agency.

In the similar way, there are many chemical processes like *burning of carbon, petrol,* etc., which take place in a particular direction only.

A process which has an urge or a natural tendency to occur either of its own or after proper initiation under a given set of conditions is known as **spontaneous process.** Spontaneous process does not mean that it takes place instantaneously. Spontaneous process may be extremely slow or it may be very fast. *Spontaneous chemical processes* are also known as **feasible** or **probable** reactions. Some of the familiar examples of spontaneous processes are listed below :

Spontaneous processes that need no initiation

(*i*) *Evaporation of water* $\quad H_2O(l) \longrightarrow H_2O\,(g)$

(*ii*) *Dissolution of sugar in water to form a solution*

$$C_{12}H_{12}O_{11}(s) + aq \longrightarrow C_{12}H_{22}O_{11}(aq)$$

(*iii*) *Reaction between nitric oxide (NO) gas with oxygen (O_2) to form nitrogen dioxide (NO_2)*

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

Spontaneous processes that need initiation

(*i*) *Hydrogen reacts with oxygen gas to produce water.* This reaction is initiated by passing an electric discharge.

$$2H_2(g) + O_2(g) \xrightarrow[\text{discharge}]{\text{electric}} 2H_2O(l)$$

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(*ii*) *Coal burns to give CO_2 when ignited.* Once burning of coal is initiated, it continues of its own.

$$C(g) + O_2(g) \xrightarrow{\text{Ignition}} CO_2(g)$$

A process which has no natural tendency or urge to occur is said to be a **non-spontaneous process.** This does not mean that non-spontaneous processes do not occur at all. Many of the non-spontaneous processes or changes may be made to occur when energy from some external source is supplied continuously throughout the change. For example, electrolysis of water. The electrolysis of water takes place only so long as electrical energy is supplied to water. Once the passage of electric current is stopped, the electrolysis of water also stops.

$$H_2O(l) \longrightarrow H_2(g) + \tfrac{1}{2}O_2(g) \textit{ non-spontaneous}$$

Spontaneity and Enthalpy change. As pointed out earlier, that spontaneous processes have an urge to occur in a particular direction under given set of conditions. This indicates that there must be some kind of *driving force* which is responsible to drag the spontaneous process in a particular direction. Let us consider some spontaneous processes in order to study the nature of this driving force.

(*i*) Water flowing down the hill ;

(*ii*) Heat flowing from the hot body to a cold body ;

(*iii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -286$ kJ ;

(*iv*) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -394$ kJ ;

(*v*) $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$; $\Delta H = -92$ kJ.

The study of above processes reveals that all of them proceed towards the *state of lower energy.* Since lower energy state is related to the stability of the systems, one could assume that the spontaneous process must be *exothermic in nature.* This leads us to conclude that criterion of spontaneity may be the **negative value of ΔH.**

Limitation of ΔH-criterion

The above conclusion fails to explain the spontaneous nature of a large number of reactions of processes in which **ΔH** is + ve or even zero. Some examples are :

(*i*) *Evaporation of water* ;

$$H_2O(l) \longrightarrow H_2O(g) \text{ ; } \Delta H = +40.6 \text{ kJ}$$

(*ii*) *Dissolution of NH_4Cl in water* :

$$NH_4Cl(s) + \text{Water} \longrightarrow NH_4^+(aq) + Cl^-(aq) \text{ ; } \Delta H = +15 \text{ kJ}$$

(*iii*) *Decomposition of mercuric oxide* :

$$HgO(s) \longrightarrow Hg(l) + \tfrac{1}{2}O_2(g) \text{ ; } \Delta H = +903 \text{ kJ}$$

(*iv*) *Intermixing of non-reacting gases* ; ΔH or $\Delta E \approx 0$

The study of above processes does not allow us to consider *negative value of ΔH* as a criterion of spontaneity and emphasises the need for the development of criterion in terms of other thermodynamic parameters.

A careful study of all the above processes (where ΔH is either positive or zero) reveals another aspect that they proceed towards a **more disordered state.** For example, consider intermixing of two non-reacting gases A and B

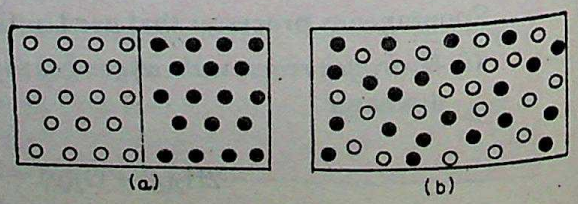

Fig. 4.6. Diffusion of gases.

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taken in two vessels which are separated by movable partition [Fig. 4.6 (*a*)]. When the partition is removed, the two gases spontaneously diffuse into each other [Fig. 4.6 (*b*)].

The intermixing of gases results due to the increase in **disorder** or **randomness** of the system. Since every system has a tendency to attain a state of maximum stability, therefore, we may propose that a *more disordered* state is *more stable.* Hence, the tendency of various systems to acquire a more random state may be responsible for the spontaneity of the process.

Let us now study the thermodynamic function which can be used to express disorder and try to develop criterion of spontaneity in terms of that parameter.

4.7. ENTROPY

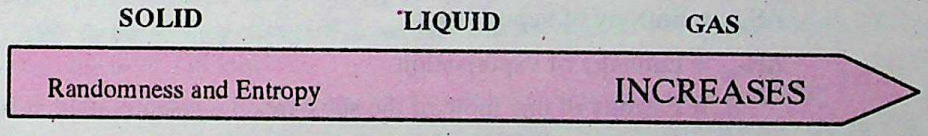
The disorder or degree of randomness in a system is represented by a thermodynamic quantity called **entropy.** It is denoted by symbol **S.** Like enthalpy and internal energy, the entropy is also a state function. When the state of the system changes, the entropy also undergoes a change. The change in entropy is represented by ΔS ($S_{final} - S_{initial}$) and is defined by the mathematical relation

$$\Delta S = \frac{q(rev)}{T}$$

where, **q(rev)** is the heat absorbed by the system in a reversible manner at the temperature **T.** If **q** is expressed in Joules (**J**) and **T** in kelvin (**K**) then the units of entropy becomes JK^{-1}.

Physical meaning of entropy

Thus, in general, in going from solid to liquid and liquid to gas, the disorder and hence entropy increases.



The **physical meaning of entropy** lies in its ability to provide a measure for degree of disorder or randomness of the system. The greater the randomness in a system, the higher is its entropy. For a given substance :

the *crystalline state* represents the state of *lowest entropy*

the *gaseous state* represents the state of *highest entropy*

the *liquid state* is the *intermediate* between the two.

In any physical or chemical process in which the system passes from *less random state* to *more random state*, the value of entropy change (ΔS) will be positive.

Now let us correlate entropy with randomness by considering the entropy changes during phase transitions.

Entropy of Phase Transition

Phase transition refers to the change of one state (*solid, liquid* or *gas*) to another. Such a change occurs at a definite temperature. For example, conversion of *solid to liquid* occurs at the *melting point,* while change of *liquid* into *vapours* occurs at the *boiling point.* The entropy change taking place during such transitions can be calculated as follows :

1. **Entropy of fusion.** Entropy of fusion may be defined as *the entropy change taking place when one mole of the substance changes from solid state into liquid state at its melting point.*

$$Solid \rightleftharpoons Liquid$$

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During this phase of transition, the system absorbs heat at constant temperature and pressure. This heat absorbed is equal to the enthalpy of fusion (ΔH_{fusion}). The entropy change during this transition can be calculated as

$$\Delta S_{fusion} = [S_l - S_s] = \frac{\Delta H_{fusion}}{T_f} \quad ...(4.10)$$

Here, ΔS_{fusion} = Entropy of fusion

ΔH_{fusion} = Enthalpy of fusion

S_l = Enthropy of one mole of liquid substance at its melting point

S_s = Entropy of one mole of solid substance at its melting point

T_f = Melting point of the substance.

Since ΔH_{fusion} is positive, therefore, ΔS_{fusion} is also positive. Hence, $S_l > S_s$, *i.e.*, entropy of liquid substance is greater than the entropy of the substance in solid state.

2. Entropy of vaporisation. Entropy of vaporisation may be defined as *the entropy change taking place when one mole of the substance changes from liquid state into vapours at its boiling point.*

$$Liquid \rightleftharpoons Gas$$

During this transition the system absorbs heat at constant temperature and pressure. This heat absorbed is equal to the enthalpy of vaporisation (ΔH_{vap}). The entropy change for this transition may be calculated as :

$$\Delta S_{vap} = S_g - S_l = \frac{\Delta H_{vap}}{T_b} \quad ...(4.11)$$

Here, ΔS_{vap} = Entropy of vaporisation

ΔH_{vap} = Enthalpy of vaporisation

S_g = Entropy of one mole of the substance in gaseous state at its boiling point

S_l = Entropy of one mole of the substance in liquid state at its boiling point

T_b = Boiling point of the substance.

Since ΔH_{vap} is positive, therefore, ΔS_{vap} is also positive. Hence, $S_g > S_l$ *i.e., entropy of the substance in gaseous state is greater than the entropy of the substance in liquid state.*

Now let us calculate entropy change during phase transition by applying equations (4.10) and (4.11).

Example 4.10. *Ethanol boils at 78.4°C, the enthalpy of vaporisation of ethanol is 42.4 kJ mol^{-1}. Calculate entropy of vaporisation of ethanol.* [A.I. CBSE (O) 1992]

Solution.

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$$

Here, $\Delta H_{vap} = 42.4 \text{ kJ mol}^{-1}$,

$T_b = 78.4°C = 351.4 \text{ K}$

$$\Delta S_{vap} = \frac{42.4 \times 1000 \text{ J mol}^{-1}}{351.4 \text{ K}} = \mathbf{120.66 \text{ JK}^{-1} \text{ mol}^{-1}}.$$

Example 4.11. *Calculate the entropy change for the conversion of 1 gram of ice to water at 273 K and one atmosphere pressure. The enthalpy of fusion of ice is 6.025 kJ mol^{-1}.* (Pb., 1992)

Solution.

$\Delta H_{fusion} = 6.025 \text{ kJ mol} = 6025 \text{ J mol}^{-1}$

$T_f = 273 \text{ K}$

$$\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T_f} = \frac{6025 \text{ J mol}^{-1}}{273 \text{ K}} = 22.1 \text{ JK}^{-1} \text{ mol}^{-1}$$

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Now entropy change for conversion of 1 mol, *i.e.*, 18 g of ice into water at 273 K = 22.1 JK^{-1}

∴ Entropy change for converting 1 g of ice into water

$$= \frac{22.1\ JK^{-1}}{18} = \mathbf{1.227\ JK^{-1}}.$$

Example 4.12. *Calculate the entropy change when 36 g of liquid water evaporates at 373 K* (ΔH_{vap} = *40.63 kJ mol*$^{-1}$).

Solution.

$$\Delta H_{vap} = 40.63\ kJ\ mol^{-1}$$

$$T_b = 373\ K$$

$$\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b} = \frac{40.63 \times 1000\ J\ mol^{-1}}{373\ K}$$

$$= 109\ JK^{-1}\ mol^{-1}$$

Entropy change for evaporation of 36 g of water

$$= \frac{109}{18} \times 36 = \mathbf{218\ JK^{-1}}.$$

REVIEW PROBLEMS

4.17. Calculate the entropy change accompanying the vaporisation of one mole of ether. The heat of vaporisation of ether is 27.2 kJ mol^{-1} and its boiling point is 308 K.

4.18. Calculate the entropy change of *n*-hexane when one mole of it evaporates at 341.7 K. Enthalpy of vaporisation of *n*-hexane is 29.0 kJ mol^{-1}.

4.19. Calculate the entropy of fusion of ice. Latent heat of fusion of ice is 334.72 Jg^{-1}.

4.20. When one mole of ethanol melts at its melting point. The entropy change is 29.4 JK^{-1} mol^{-1}. If enthalpy of fusion of ethanol is 4.6 kJ mol^{-1}, what is the melting point of ethanol ?

4.21. ΔS_{vap} of acetone is 93.00 JK^{-1} mol^{-1}. If boiling point of acetone is 56°C. Calculate the heat required for vaporisation of 1 g of acetone.

4.22. The following data is known about the melting of KCl. ΔH = 7.25 kJ mol^{-1} and ΔS = 0.007 kJ K^{-1} mol^{-1}. Calculate the melting point of KCl. [*H.P. (Sc.) 1993*]

4.23. Calculate the entropy change involved in the vaporisation of water at 373 K. The latent heat of vaporisation of water is 2.52 kJ g^{-1}. (*Haryana Board 1995*)

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PREDICTING THE SIGN OF ΔS

As pointed out earlier, the processes in which entropy of products is greater than the entropy of reactants, have positive ΔS. Such processes are accompanied by increase in randomness.

In many reactions it becomes possible to predict the sign of ΔS by simply observing the reactants and products. If the products are more random than reactants, ΔS is positive and if products are less random than reactants, ΔS is negative. Now, let us consider some reactions and predict the sign of ΔS.

(*i*) $$C(s) + \frac{1}{2}O_2(g) \longrightarrow CO(g)$$

In this reaction, the product is more random than the reactants because the product molecules are in gaseous state whereas one of the reactants is in solid state. So ΔS would be positive for this reaction.

(*ii*) $$2SO_3(g) \longrightarrow 2SO_2(g) + O_2(g)$$

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In this reaction also products are more random than reactant because in products more molecules are present in gaseous state than in the reactant. So ΔS is + ve.

(*iii*) $NaCl(s) + H_2O(l) \longrightarrow Na^+(aq) + Cl^-(aq)$

This process is also accompanied by increase in randomness because Na^+ and Cl^- ions are free to move in solution whereas they are not free to move in solid NaCl. Hence, ΔS is positive for this type of dissolution processes.

Spontaneity and Entropy

In order to establish relationship between entropy and spontaneity let us again consider some spontaneous processes :

(*a*) When non-reacting gases are allowed to intermix, the process continues till each gas is distributed throughout the entire available space uniformly.

(*b*) If a drop of ink is added to water in a beaker, the colour of the ink starts spreading and ultimately the whole amount of water acquires the uniform colour.

(*c*) If a tray containing white and red balls arranged separately in two opposite corners is shaken, the balls mix up and acquire most disordered arrangement.

(*d*) If some water is placed in a well insulated vessel fitted with manometer, pressure is slowly developed in the vessel due to evaporation of water.

A careful study of the above spontaneous processes reveals the following facts :

1. In each of the above processes, the system can be assumed to be **isolated** because it does not involve any exchange of matter or energy with the surroundings.
2. In each of the above processes, the system is tending to attain more disordered state. In other words, each process involves increase of randomness. In terms of *entropy*, we can say that in each of these processes, entropy of the final state is higher than that of initial state,

i.e., $$S_{final} > S_{initial}$$

or $$\Delta S = (S_{final} - S_{initial}) > 0$$

The above discussion allows us to make a generalised statement that in **isolated systems,** ***the process will be spontaneous only if the entropy change of the system is positive.***

or $$\Delta S_{sys} > 0 \text{ (For spontaneity is isolated systems)} \quad ...(4.12)$$

The equation (4.12) works very well in predicting the spontaneity in isolated systems, but it fails to predict the spontaneity in **non-isolated systems.** For example, ΔS_{sys} for freezing of water, $H_2O(l) \longrightarrow H_2O(s)$ at 272 K and 1 atm pressure is negative ($-21.85\ JK^{-1}\ mol^{-1}$) indicating that the process is non-spontaneous. But we observe that freezing of water is spontaneous at 272 K and 1 atm. pressure.

The reason for the above failure lies in the fact that the non-isolated systems are in direct contact with the surroundings, therefore, for predicting the spontaneity of a process in case of non-isolated systems it is essential to consider the total entropy change of the universe, *i.e.*, entropy change of the system (ΔS_{sys}) as well as the entropy change of the surroundings (ΔS_{surr}). If the entire universe is taken as isolated system, then, for any spontaneous process occurring in the universe, the total entropy change, ΔS_{Total} or $\Delta S_{universe}$ should be positive.

Thus, for spontaneous change,

$$\Delta S_{Total} > 0 \quad ...(4.13)$$

or $$\Delta S_{universe} > 0 \quad ...(4.14)$$

or $$\Delta S_{sys} + \Delta S_{surr} > 0 \quad ...(4.15)$$

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Equation (4.15) also justifies the spontaneity of freezing of water at 272 K and 1 atmosphere pressure. For the process,

$$\Delta S_{sys} = -21.85\ JK^{-1}\ mol^{-1}$$

$$\Delta S_{surr.} = +21.93\ JK^{-1}\ mol^{-1}$$

$$\therefore \quad \Delta S_{total} = \Delta S_{sys} + \Delta S_{surr.}$$

$$= 21.85 + 21.93 = +0.07\ JK^{-1}\ mol^{-1}$$

The positive value of ΔS_{total} makes the process spontaneous.

The Statement of Second Law of Thermodynamics

The relation (4.15) forms the basis of most useful form of the Second Law of Thermodynamics which states that

The entropy of the universe always increases in the course of every spontaneous (natural) change.

By combining the statements of First and Second Laws of Thermodynamics, we conclude that

in any natural or spontaneous process the energy of universe remains constant but the entropy of universe always increases.

Entropy Change and Equilibrium

We have learnt that for spontaneous processes, $\Delta S_{total} > 0$. The careful study of the spontaneous processes reveals another important aspect that each of them gradually and ultimately passes into the state of equilibrium*. For example, in intermixing of gases, the process of intermixing continues till a uniform mixture is formed. Similarly, in evaporation of water in closed vessel, soon a state of equilibrium is reached. Although these processes are favoured by increase in the value of ΔS_{total}, yet, no further increase in entropy occurs once the equilibrium is established. This leads us to conclude that :

At equilibrium, $\Delta S_{total} = 0$ ...(4.16)

Following the above discussion, the **entropy criterion** can be summed up as follows :

$\Delta S_{Total} > 0$;	*process is spontaneous*
$\Delta S_{Total} = 0$;	*equilibrium state*
$\Delta S_{Total} < 0$;	*process is non-spontaneous*

Let us illustrate the application of the **entropy criterion** to decide the spontaneity of *Water* $\rightleftharpoons$ *Ice* transformation. The relevent entropy values are given in Table 4.3 for three different temperatures 272, 273 and 274 K respectively.

Table. 4.3. Entropy Changes for the Transformation $H_2O(l) \longrightarrow H_2O(s)$ at 1 atm.

Temperature (K)	ΔS_{system} $(JK^{-1}\ mol^{-1})$	$\Delta S_{surroundings}$ $(JK^{-1}\ mol^{-1})$	ΔS_{total} $(JK^{-1}\ mol^{-1})$
272	– 21.85	+ 21.93	+ 0.08
273	– 21.99	+ 21.99	0
274	– 22.13	+ 22.05	– 0.08

*The word **equilibrium** used here, does not refer to *chemical equilibrium* only. It includes *thermal equilibrium* and also *mechanical equilibrium as well.*

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(*i*) *At 272 K* ; freezing is spontaneous because ΔS_{total} is + ve.

(*ii*) *At 274 K* ; freezing is not spontaneous because ΔS_{total} is – ve but the reverse change, *i.e.* melting is spontaneous.

(*iii*) *At 274 K*, ΔS_{total} is **zero.** Thus, ice and water are in equilibrium and no net change is observed.

4.8. FREE ENERGY AND FREE ENERGY CHANGE

In the previous section, we developed the **entropy criterion for spontaneity** which reveals that for a process to be spontaneous, $\Delta S_{total} > 0$ or $\Delta S_{sys} + \Delta S_{surr} > 0$. One of the **limitation** of entropy criterion, lies in the fact that in order to decide the spontaneity of a process we have to consider the change in the entropy of the system as well as surroundings. However, while dealing with the chemical reactions, it is quite difficult to consider the change in the entropy of the surroundings every time. So it is quite desirable to introduce some function which can be applied to system only but it automatically takes into account, the entropy change of the surroundings, *i.e.*, it should be able to give the idea of the spontaneity of the process alone at the given set of conditions. *Gibb's free energy* (G) is one such thermodynamic function which helps in the development of the criterion of spontaneity or feasibility of a process. Free energy refers to the capacity of the system to do the useful work. It may be defined as **the amount of energy available from a system at particular set of conditions that can be put into useful work.** Mathematically, free energy (G) is defined by the following relation :

$$G = H - TS \quad ...(4.17)$$

where H = Enthalpy of the system

S = Entropy of system

T = Temperature

We know that $H = E + PV$

$$\therefore \quad G = E + PV - TS \quad ...(4.18)$$

The change in free energy (ΔG) during the process can be expressed as.

$$\Delta G = \Delta E + \Delta(PV) - \Delta(TS) \quad ...(4.19)$$

If the process is carried out at *constant pressure* and *constant temperature* the terms

$\Delta(PV)$ becomes $P\Delta V$ and $\Delta(TS)$ becomes $T\,\Delta S$.

Thus, we can write $$(\Delta G)_{T,\,P} = \Delta E + P\Delta V - T\Delta S \quad ...(4.20)$$

We know that at constant temperature and constant pressure,

$$\Delta E + P\Delta V = \Delta H$$

Thus, $$\Delta G_{T,\,P} = \Delta H - T\Delta S \quad ...(4.21)$$

The equation (4.21) is known as **Gibb's Helmholtz equation.**

Spontaneity and Free Energy Change

Let us now develop the criterion of spontaneity in terms of free energy change. We have learnt earlier that total entropy change during the process is given by

$$\Delta S_{total} = \Delta S_{system} + \Delta S_{surr.} \quad ...(4.22)$$

Consider a process being carried out at constant temperature and constant pressure. Suppose heat equal to **q** is lost by surroundings and gained by the system at temperature **T**. Then the entropy change of the surroundings is given by

$$\Delta S_{surr.} = \frac{-q}{T} \quad ...(4.23)$$

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Negative sign before **q** indicates that the heat has been lost by the surroundings. Now heat gained by system at constant temperature and pressure **q** represents its enthalpy change (ΔH). Therefore,

$$\Delta S_{surr.} = \frac{-q}{T} = \frac{-\Delta H_{(system)}}{T} \qquad (\because \; q_p = \Delta H_{system})$$

Substituting this value in equation (4.22), we get

$$\Delta S_{total} = \Delta S_{system} - \frac{\Delta H_{(system)}}{T}$$

Multiplying throughout by **T**

$$T\Delta S_{total} = T\Delta S_{system} - \Delta H_{system}$$

$$-T\Delta S_{total} = \Delta H_{system} - T\Delta S_{system}$$

or

$$-T\Delta S_{total} = \Delta G_{system} \qquad ...(4.24) \quad (\because \; \Delta H - T\Delta S = \Delta G)$$

The equation (4.24) forms the basis for the criterion of spontaneity in terms of free energy change of the system only. For example, for a process to be spontaneous ΔS_{total} is **positive.** So that ΔG_{system} is **negative.**

Thus, *for a process at a particular temperature and pressure to be spontaneous the free energy of the system must be decrease i.e.,* $\Delta G_{T,P} < 0$.

Let us now summarize the free energy criteria of spontaneity, as

(*i*) If ΔS_{total} is *positive* ; $\Delta G_{T,P}$ is *negative ; The process will be* **spontaneous.**

(*ii*) If $\Delta S_{total} = 0$; $\Delta G_{T,P} = 0$; The process will represent **equilibrium.**

(*iii*) If ΔS_{total} is *negative* ; $\Delta G_{T,P}$ is *positive ; The process will be* **non-spontaneous.**

Conditions for ΔG to be negative. Let us now formulate the conditions for ΔG to be negative. It can be done by considering *Gibb's Helmholtz equation.*

$$\Delta G = \Delta H - T\Delta S$$

(*i*) Both the *energy factor* as well as *entropy factor* are favourable, *i.e.*, ΔH is *negative* and ΔS is *positive.* Under these conditions ΔG would certainly be negative and the process would occur spontaneously.

(*ii*) *Energy factor favours* but *entropy factor opposes, i.e.* ΔH is *negative* and ΔS is also *negative.* Under these conditions ΔG would be **negative** if ΔH is **greater than** TΔS in magnitude.

(*iii*) *Energy factor opposes* but *entropy factor favours, i.e.,* ΔH is *positive* and ΔS is also *positive.* Under these conditions ΔG would be **negative** if TΔS is **greater than** ΔH magnitude.

These conditions have been summarized in Table 4.4.

Table 4.4. Conditions for negative value of ΔG or for spontaneity of a reaction

Sign of ΔH	*Sign of ΔS*	*Sign of ΔG, occurrence of reaction*
–	+	– Ve (spontaneous)
+	+	– Ve (If TΔS > ΔH)
–	–	– Ve (If ΔH > TΔS)

Effect of Temperature on Feasibility of a Process

Gibb's-Helmholtz equation helps us in predicting the feasibility of a process at a particular temperature. A process which is spontaneous at a particular temperature may becomes non-spontaneous at some other

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temperature. Similarly, a process which is non-spontaneous at a particular temperature may becomes spontaneous at some other temperature. Temperature effects feasibility of endothermic and exothermic reactions in different ways as discussed below :

(*a*) **For endothermic processes,** ΔH is **positive** (*opposing*) and hence, for the process to be spontaneous $T\Delta S$ must be **positive** (favourable) and greater than ΔH. With increase in temperature the magnitude of the favourable factor, $T\Delta S$ increase whereas ΔH does not change much. On the other hand, with decrease in temperature $T\Delta S$ decreases and at certain temperature may become less than ΔH in magnitude. At this stage, the ΔG would become positive and the process would no longer be spontaneous. So *for endothermic process* **higher temperatures** *favour the spontaneity or feasibility of the process.*

(*b*) **For exothermic processes,** ΔH is **negative** (*favourable*) and $T\Delta S$ would generally be **negative** (*opposing*). For such reactions to be spontaneous, the magnitude of ΔH must be greater than $T\Delta S$. With increase in temperature, the opposing factor $T\Delta S$ increases whereas favourable factor ΔH remains almost constant. Thus, at some higher temperature $T\Delta S$ may become greater than ΔH. At this stage, ΔG would become positive and the process would no longer be spontaneous. So *for exothermic processes* **low temperatures** *favour the spontaneity of the process.*

In order to understand the application of Gibb's-Helmholtz equation in predicting the spontaneity of process, let us solve some numerical problems.

Example 4.13. *Calculate the standard free energy change, $\Delta G°$ for the reaction*

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

Given that the standard enthalpy change and standard entropy change for the reaction are 52.0 kJ and 165.2 JK^{-1} respectively. Is this reaction spontaneous at 298 K ?

Solution. $\Delta G° = \Delta H° - T\Delta S°$

Here, $\Delta H° = 52.0$ kJ

$\Delta S° = 165.2\ JK^{-1}$

$T = 298$ K

$$\Delta G° = \Delta H° - T\Delta S°$$

$$= 52.0 - \frac{298 \times 165.2}{1000} = +2.7 \text{ kJ.}$$

Since $\Delta G°$ has a positive value, therefore, the reaction is not spontaneous at 298 K (standard condition).

Example 4.14. *For the reaction,*

$$N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$$

$$\Delta H = -95.4 \text{ kJ and } \Delta S = -198.3\ JK^{-1}$$

Calculate the temperature at which free energy change (ΔG) is equal to zero. Predict the nature of the reaction at this temperature and above it.

Solution. $\Delta G = \Delta H - T\Delta S$

When $\Delta G = 0$

$$\Delta H - T\Delta S = 0 \quad \text{or} \quad \Delta H = T\Delta S$$

$$T = \frac{\Delta H}{\Delta S} = \frac{-95.4 \times 1000 \text{ J}}{-198.3\ JK^{-1}} = \mathbf{481\ K.}$$

At this temperature the reaction would be in equilibrium. With increase in temperature the opposing factor $T\Delta S$ would become more and hence, ΔG would become positive and the reaction would become non-spontaneous (*i.e.*, will occur). The reaction would be spontaneous at the temperatures below 481 K.

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REVIEW PROBLEMS

4.24. ΔH and ΔS for the vaporization of water at 1 atmosphere are 40.63 kJ mol^{-1} and 108.8 JK^{-1} respectively. Calculate the temperature at which the free energy change for this transformation will be zero. Predict giving reasons, the sign of free energy change (ΔG) above this temperature. *(CBSE 1993)*

4.25. For the reaction $A(g) + 3B(g) \longrightarrow 2C(g)$, the enthalpy change is – 100.32 kJ mol^{-1} and ΔS is – 0.1672 kJ K^{-1} mol^{-1}. Predict whether the reaction is feasible at 298 K or not.

4.26. Calculate the free energy change for the dissolution of potassium nitrate in water at 289 K

$$KNO_3(s) + \text{Water} \longrightarrow K^+(aq) + NO_3^-(aq)$$

$$\Delta H° = 34 \text{ kJ mol}^{-1}$$

$$\Delta S° = 0.116 \text{ kJ K}^{-1} \text{ mol}^{-1}.$$

4.27. For the reaction $Ag_2O(s) \longrightarrow 2Ag(s) + \frac{1}{2}O_2(g)$; $\Delta H = 30.56$ kJ mol^{-1} and $\Delta S = 0.066$ kJ K^{-1} mol^{-1} (at 1 atm). Calculate the temperature at which ΔG is equal to zero. Also predict the direction of the reaction at (*i*) this temperature, and (*ii*) below this temperature. *(A.I. CBSE 1993 ; CBSE 1992)*

4.28. From the following values of ΔH and ΔS decide whether or nor these reactions will be spontaneous at 298 K.

Reaction A : $\Delta H = -10.5 \times 10^3$ J mol^{-1} ;

$\therefore$ $\Delta S = +31$ J K^{-1} mol^{-1} *(Pb. 1993)*

Reaction B : $\Delta H = -11.7 \times 10^{-3}$ J mol^{-1} ;

$\Delta S = -105$ J K^{-1} mol^{-1}.

4.29. ΔH and ΔS for $Br_2(l) + Cl_2(g) \longrightarrow 2BrCl(g)$ are + 29.37 kJ mol^{-1} and 104.0 J K^{-1} respectively. Above what temperature will this reaction become spontaneous. *[A.I. CBSE 1992]*

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Standard Free Energy Change ($\Delta G°$)

The standard free energy change is defined as the ***free energy change for a process in which reactants in their standard states are converted into the products in their standard states.*** It is denoted by the symbol $\Delta G°$. The standard free energy change is related to the standard enthalpy change by the relation

$$\Delta G° = \Delta H° - T\Delta S°$$

where, $\Delta H°$ and $\Delta S°$ represent the standard enthalpy change and standard entropy change during the process respectively.

Like $\Delta H°$, the standard free energy change ($\Delta G°$) of a reaction can be calculated from the standard free energy of formation of the products and that of the reactants. The **standard free energy of formation** ($\Delta G_f°$) is defined as the ***free energy change taking place when 1 mole of the compound is formed from its constituent elements in the standard states.*** It may be noted that the standard free energy of formation ($\Delta G_f°$) of *elementary substances* in their most stable form is taken to be *zero*. The standard free energies of formation of some substances are given in Table 4.5.

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Table 4.5. Standard Gibbs Free Energies of Formation ΔG_f° at 298 K

Substance	ΔG_f° (298) ($kJ\ mol^{-1}$)	*Substance*	ΔG_f° (298) ($kJ\ mol^{-1}$)
$Al_2O_3(g)$	– 1576.41	$H_2O(g)$	–.228.6
$Br_2(l)$	0.0	$N_2(g)$	0.0
$Br(g)$	3.1	$N(g)$	455.6
$Br_2(g$	82.4	$NO(g)$	86.7
$Br^-(aq)$	– 102.8	$NO_2(g)$	51.84
C(graphite)	0.0	$NaCl(s)$	– 384.05
C(diamond)	2.8	$O_2(g)$	0.0
$CH_4(g)$	– 50.8	$O(g)$	230.1
$C_2H_6(g)$	– 32.9	$O_3(g)$	163.4
$C_2H_2(g)$	209.2	P(white)	0.0
$C_6H_6(l)$	124.5	P(red)	– 12.0
$CO(g)$	– 137.3	S(rhombic)	0.0
$CO_2(g)$	– 394.4	$SO_2(g)$	– 300.4
$Cl(g)$	105.4	$H_2SO_4(l)$	– 690.0
$Fe_2O_3(s)$	748.0	$SO_4^{2-}(aq)$	– 742.2
$H(g)$	203.3	$H_2S(g)$	– 33.0
$H_2O(l)$	– 237.2	$ZnO(s)$	– 318.19

The standard free energy change of a reaction can be calculated from the the knowledge of standard free energy of formation of various substances as described below :

$$\Delta G^\circ = \Sigma\Delta G_f^\circ\ (products) - \Sigma\Delta G_f^\circ\ (reactants) \quad ...(4.25)$$

$$= \left[\begin{array}{c}\text{Sum of standard free energies}\\ \text{of formation of products}\end{array}\right] - \left[\begin{array}{c}\text{Sum of standard free energies}\\ \text{of formation of reactants}\end{array}\right]$$

For example, for a reaction ; $aA + bB \longrightarrow lL + mM$,

the standard free energy can be calculated as

$$\Delta G^\circ = \Sigma\Delta G_f^\circ\ (products) - \Sigma\Delta G_f^\circ\ (reactants)$$

$$= [l\Delta G_f^\circ(L) + m\Delta G_f^\circ(M)] - [a\Delta G_f^\circ(A) + b\Delta G_f^\circ(B)].$$

Example 4.15. *Calculate the standard free energy change for the reaction given below :*

$$C_2H_2(g) + 2H_2(g) \longrightarrow C_2H_6(g)$$

from the data given in Table 4.5.

Solution. The standard free energy change of the reaction is given by

$$\Delta G^\circ = \Sigma\Delta G_f^\circ\ (\text{products}) - \Sigma\Delta G_f^\circ\ (\text{reactants})$$

$$= (-32.9\ kJ\ mol^{-1}) - (209.2 + 0) = -32.9 - 209.2 = \mathbf{242.1\ kJ\ mol^{-1}}.$$

Example 4.16. *Calculate the standard free energy change for the following reaction :*

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

Given that ΔG_f° for $Cu^{2+}(aq)$ and $Zn^{2+}(aq)$ as 65 $kJ\ mol^{-1}$ and – 147.2 $kJ\ mol^{-1}$ respectively.

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Solution. The given redox reaction is

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

Now
$$\Delta G^\circ = \Sigma\Delta G_f^\circ \text{ (products)} - \Sigma\Delta G_f^\circ \text{ (reactants)}$$
$$= [0 + (-147.2)] - [0 + 65.00]$$
$$= -147.2 - 65.00 = \mathbf{-212.2\ kJ.}$$

REVIEW PROBLEMS

4.30. Calculate the standard free energy change for the reaction $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(l)$. Given ΔG_f° for $NH_3(g)$, $NO(g)$ and $H_2O(l)$ as – 16.3, + 86.5 and – 237.0 kJ mol^{-1} respectively.

4.31. Calculate the standard free energy change for the reaction $2SO_2(g) + O_2(g) \longrightarrow 2SO_3(g)$. The values of ΔG_f° for $SO_2(g)$ and $SO_3(g)$ are – 300.2 kJ mol^{-1} and – 371.1 kJ mol^{-1} respectively.

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Standard Free Energy Change and Equilibrium Constant

The standard free energy change of a chemical reaction is related to its equilibrium constant by the relation

$$\Delta G^\circ = \mathbf{-2.303\ RT \log K} \qquad ...(4.26)$$

This relation helps us to calculate the value of ΔG° if K is known and *vice versa.*

Example 4.17. *The equilibrium constant for a reaction*

$$CO_2(g) + H_2(g) \rightleftharpoons CO(g) + H_2O(g)$$

is 73. Calculate the value of standard free energy change.

Solution.
$$\Delta G^\circ = -2.303\ RT \log K$$
$$= -2.303 \times (8.314\ JK^{-1}\ mol^{-1})\ (298\ K)\ (\log 73)$$
$$= -2.303 \times 8.314 \times 298 \times 1.8633$$
$$= -10631.7\ J\ mol^{-1} = \mathbf{-10.632\ kJ\ mol^{-1}}.$$

Example 4.18. *Calculate the standard entropy change for a reaction* $X \rightleftharpoons Y$ *if the value of* $\Delta H^\circ = 28.40$ *kJ and equilibrium constant is* 1.8×10^{-7} *at 298 K.*

Solution. We Know that
$$\Delta G^\circ = -2.303\ RT \log K_{eq}$$
$$= -2.303 \times (8.314\ JK^{-1}\ mol^{-1})\ (298\ K)(\log K_{eq})$$
$$= -2.303 \times 8.314 \times 298 \times \log (1.8 \times 10^{-7})$$
$$= 38.484\ kJ\ mol^{-1}$$

Also
$$\Delta G^\circ = \Delta H^\circ - T\Delta S^\circ$$

or
$$\Delta S^\circ = \frac{\Delta H^\circ - \Delta G^\circ}{T}$$
$$= \frac{28.40\ kJ\ mol^{-1} - 38.498\ kJ\ mol^{-1}}{298\ K}$$
$$= -0.0338\ kJ\ mol^{-1}\ K^{-1} = \mathbf{-33.8\ JK^{-1}\ mol^{-1}}.$$

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REVIEW PROBLEMS

4.32. Calculate the equilibrium constant for a reaction $2NOCl(g) \rightleftharpoons 2NO(g) + Cl_2(g)$ at 400 K. The value of $\Delta G°$ for the reaction is 28.4 kJ mol^{-1}.

4.33. Calculate $\Delta G°$ for a reaction at 298 K

$$PCl_5(g) \rightleftharpoons PCl_3(g) + Cl_2(g) \qquad K = 1.8 \times 10^{-7}.$$

4.34. Calculate entropy change ($\Delta S°$) for the reaction $P \rightleftharpoons Q$; $\Delta H° = 28.40$ kJ. The equilibrium constant for a reaction is given to be 1.8×10^{-7} at 298 K.

4.35. A certain hypothetical reaction $A_2(l) + B_2(l) \rightleftharpoons 2AB(l)$ is found have value of equilibrium constant equal to 4. Calculate the value of standard free energy change.

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Physical Significance of Free Energy

In order to understand the physical significance of free energy, let us consider the relationship between *heat* (**q**) and *work* (**w**). According to *First Law of Thermodynamics*

$$\Delta E = q + w$$

Here, **w** includes the *pressure volume* work ($-P\Delta V$) as well as non-PV work. Therefore, the above relation can be written as

$$\Delta E = q - P\Delta V + w_{non\text{-}exp.}$$

$$q = \Delta E + P\Delta V - w_{non\text{-}exp.}$$

$$= \Delta H - w_{non\text{-}exp.} \qquad ...(4.27)$$

Now, by definition, for a change taking place under isothermal and reversible conditions, the entropy change ΔS is given by

$$\Delta S = \frac{q}{T} \quad \text{or} \quad q = T\Delta S \qquad ...(4.28)$$

Substituting this value of **q** in equation (4.27),

$$T\Delta S = \Delta H - w_{non\text{-}exp.}$$

or $$\Delta H - T\Delta S = w_{non\text{-}exp.}$$

or $$\Delta G_{T,P} = w_{non\text{-}exp.} \qquad ...(4.29)$$

or $$-\Delta G_{T,P} = -w_{non\text{-}exp.}$$

Decrease in free energy = non-expansion work done by the system

Thus, for the process taking place at constant temperature and constant pressure the **decrease in free energy** *provides measure of* **non-expansion** *work done by the system.* The non-expansion work can be put to useful purposes and is also called *useful work.* Hence, the free energy (G) of a system is a measure of its capacity to do useful work. It is part of the total energy of the system that is free for conversion into useful work. That is why, it is called **free energy.**

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4.9. THIRD LAW OF THERMODYNAMICS AND ABSOLUTE ENTROPIES

We know that entropy is a measure of disorder or randomness of any system. Disorder in any substance depends upon

(*i*) *its mass,*

(*ii*) *its molecular structure, and*

(*iii*) *conditions of temperature and pressure.*

The increase in temperature of the substance at constant pressure increases its disorder. Conversely, if the temperature of the substance deceases its disorder also decreases. Eventually, as the temperature approaches *zero* kelvin, the disorder also approaches zero and the substance tends to become perfectly ordered. Based upon the above facts Nernst formulated third law of thermodynamics in 1906. The law states that,

At absolute zero, the entropy of a perfectly crystalline substance is zero.

Utility of Third Law

The absolute values of the entropies of various substances at room temperature can be determined by application of third law of thermodynamics as discussed below : The method involves the measurement of the values of heat capacity (C_p) of the substance at different temperatures.

If S_0 be the entropy of the substance at 0 kelvin and S be its entropy at T kelvin, then

$$\Delta S = (S - S_0) = \int_0^T \frac{C_p}{T} dT$$

According to third law, S_0 *i.e.*, entropy at 0 kelvin = 0

$$\therefore \quad S = \int_0^T \frac{C_p}{T} dT \qquad ...(4.30)$$

The value of the integral in equation (4.30) can be determined from the graph obtained by plotting various values of C_p against temperature (T). The area of the curve between 0 K and T K gives the value of integral and thus value of S at temperature T can be calculated.

When entropy of the one mole of a substance is expressed at 298 K and 1 atmosphere pressure, it is called standard entropy of the substance and is denoted by S°. The values of standard entropies of various substances are given in Table 4.6.

Table 4.6. Absolute Entropies at 298 K and 1 Atmospheric Pressure

Substance	*S°* ($JK^{-1}\ mol^{-1}$)	*Substance*	*S°* ($JK^{-1}\ mol^{-1}$)
$H_2(g)$	130.6	$HBr(g)$	198.5
$F_2(g)$	203.3	$HI(g)$	206.3
$Cl_2(g)$	223.0	$NH_3(g)$	192.5
$Br_2(l)$	152.3	$CH_4(g)$	186.2
$I_2(s)$	116.7	$C_2H_4(g)$	219.5
$O_2(g)$	205.03	$C_6H_6(g)$	173.3
S(rhombic)	31.9	$SO_2(g)$	248.5
$N_2(g)$	191.5	$CO_2(g)$	213.6

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Substance	$S°$ ($JK^{-1}\ mol^{-1}$)	*Substance*	$S°$ ($JK^{-1}\ mol^{-1}$)
C(graphite)	5.69	$NO_2(g)$	240.5
C(diamond)	2.4	$NaCl(s)$	72.38
$Al(s)$	28.3	$CaCO_3(s)$	92.9
$H_2O(g)$	188.7	$Al_2O_3(s)$	51.0
$H_2O(l)$	69.96	$CO(g)$	197.6
$HCl(g)$	186.7	$HgO(s)$	72.0

Calculation of ΔS°. The standard entropy charge (ΔS°) of chemical reaction can be calculated from the standard entropies various substances.

$$\Delta S° = \Sigma S°\ (products) - \Sigma S°\ (reactants)$$

For example for a chemical reaction

$$aA + bB \longrightarrow lL + mM$$

$$\Delta S° = [lS_{(L)}° + mS_{(M)}°] - [aS_{(A)}° + bS_{(B)}°]$$

Example 4.19. *Using Table 4.6, calculate the values of ΔS° for the following reactions :*

(*a*) $H_2(g) + I_2(s) \longrightarrow 2HI(g)$

(*b*) $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$.

Solution. (*a*)

$$\Delta S° = \Sigma S°\ (\text{products}) - \Sigma S°\ (\text{reactants})$$
$$= 2S°_{HI} - (S°_{H_2} + S°_{I_2})$$
$$= 2 \times 206.3 - (130.6 + 116.7)$$
$$= 412.6 - 247.3 = \mathbf{165.3\ JK^{-1}\ mol^{-1}}.$$

(*b*)

$$\Delta S° = \Sigma S°\ (\text{products}) - \Sigma S°\ (\text{reactants})$$
$$= S°_{CO_2} - (S°_{CO_2} + \tfrac{1}{2} S°_{O_2})$$
$$= 213.6 - (197.6 + \tfrac{1}{2} \times 205.03)$$
$$= 213.6 - 300.1 = \mathbf{-86.5\ JK^{-1}\ mol^{-1}}.$$

REVIEW PROBLEMS

4.36. Using data given in Table 4.6, calculate the entropy change for the following reactions :

(*a*) $CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$

(*b*) $CH_4(g) + H_2O(g) \longrightarrow CO(g) + 3H_2(g)$

4.37. Calculate the entropy change for the reaction

$$SO_2(g) + \tfrac{1}{2}O_2(g) \longrightarrow SO_3(g)$$

S° for $SO_2(g)$, $O_2(g)$ and $SO_3(g)$ are 248.5, 205, 256.2 JK^{-1} respectively.

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MISCELLANEOUS EXAMPLES

Example 4.20. *Using the data (all value in kilo calories at 25°C) given below, calculate the bond energies of C—H and C—C bonds.* $\Delta H^\circ_{combustion}$ *of ethane and propane are – 372 and – 530 k cal mol*$^{-1}$ *respectively,* ΔH_f° *of* $CO_2(g)$ *and* $H_2O(l)$ *are – 94.0 and – 68 k cal mol*$^{-1}$, ΔH° *for C(graphite)* $\longrightarrow$ *C(g) is + 172 k cal and* ΔH_{H-H} *is 104.0 k cal.* (I.I.T. J.E.E. 1990)

Solution. The thermochemical equations representing the above data are :

1. $C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta H_1 = -372.0$ kcal
2. $C_3H_8(g) + 5O_2(g) \longrightarrow 3CO_2(g) + 4H_2O(l)$; $\Delta H_2 = -530.0$ kcal
3. $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H_3 = -68.0$ kcal
4. $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H_4 = -94.0$ kcal
5. $H_2(g) \longrightarrow 2H(g)$; $\Delta H_5 = +104.0$ kcal
6. $C(\text{graphite}) \longrightarrow C(g)$; $\Delta H_6 = +172$ kcal

Consider the reactions

7. $CH_3 - CH_3(g) \longrightarrow 2C(g) + 6H(g)$; $\Delta H_7 = ?$
8. $CH_3CH_2CH_3(g) \longrightarrow 3C(g) + 8H(g)$; $\Delta H_8 = ?$

Now multiply equation 6 by 2, equation 5 by 3 and add these to equation 1. From the resulting expression subtract equation 4 by multiplying with 2 and equation 3 by multiplying with 3.

Thus, $(2 \times eq\,6 + 3 \times eq\,5 + eq\,1 - 2 \times eq\,4 - 3 \times eq\,3)$ gives us

$$CH_3 - CH_3(g) \longrightarrow 2C(g) + 6H(g) ;$$

$$\Delta H_7 = 2 \times 172 + 3 \times 104 + (-372) - 1(-94.0) - 3(-68)$$
$$= 676 \text{ kcal.}$$

ΔH_7 refers to the enthalpy change involving cleavage of one C—C bond and 6 C—H bonds, *i.e.*

$$\Delta H_7 = \Delta H_{C-C} + 6\Delta H_{C-H} = 676 \text{ kcal} \quad ...(i)$$

Similarly $3 \times eq\,6 + 4 \times eq\,5 + eq\,2 - 3 \times eq\,4 - 4 \times eq\,3$ gives us

$$CH_3CH_2CH_3(g) \longrightarrow 3C(g) + 8H(g) ;$$

$$\Delta H_8 = 3 \times (172) + 4 \times 104 + (-530) - 3(-94.0) - 4(-68.0)$$
$$= 956 \text{ kcal}$$

ΔH_8 refers to the enthalpy change involving cleavage of two C—C bonds and 8 C—H bonds *i.e.*,

$$\Delta H_8 = 2\Delta H_{C-C} + 8\Delta H_{C-H} = 956 \text{ kcal} \quad ...(ii)$$

Multiply eq. (*i*) by 2 and subtract eq. (*ii*) from it

$$2\Delta H_7 - \Delta H_8 = 2\Delta H_{C-C} - 2\Delta H_{C-C} + 12\Delta H_{C-H} - 8\Delta H_{C-H}$$

$$2 \times 676 - 956 = 4\,\Delta H_{C-H}$$

or $$\Delta H_{C-H} = \frac{396}{4} = \mathbf{99 \text{ kcal mol}^{-1}}$$

According to eq. (*i*), $\Delta H_{C-C} + 6\Delta H_{C-H} = 676$

$$\Delta H_{C-C} = 676 - 6 \times \Delta H_{C-C}$$
$$= 676 - 6 \times 99 = \mathbf{82 \text{ kcal mol}^{-1}}.$$

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Example 4.21. *Calculate the resonance energy of N_2O from the following data :*

ΔH_f° of N_2O = 82 kJ mol^{-1}, Bond energies of N ≡ N, N = N, O = O and N = O bonds are 946, 418, 498 and 607 kJ mol^{-1} respectively. (Roorkee Ent. 1991)

Solution.

Calculation of expected value of ΔH_f° of N_2O from given data

$$N \equiv N(g) + \frac{1}{2}O = O(g) \longrightarrow \overline{N} = \overset{+}{N} = O(g)$$

The ΔH° of the above reaction which represents the formation of $N_2O(g)$ is given by

$$\Delta H^\circ = \begin{bmatrix}\text{Energy required to}\\ \text{break the bonds}\end{bmatrix} - \begin{bmatrix}\text{Energy released for}\\ \text{forming the bonds}\end{bmatrix}$$

$$= (\Delta H_{N \equiv N} + \frac{1}{2}\Delta H_{O = O}) - (\Delta H_{N=N} + \Delta H_{N = O})$$

$$= (946 + \frac{1}{2} \times 498) - (418 + 607)$$

$$= 1195 - 1025 = 170 \text{ kJ mol}^{-1}$$

Observed value of ΔH_f° of $N_2O(g)$ = 82 kJ mol^{-1}

Resonance Energy $= \begin{pmatrix}\text{Expected value}\\ \text{of } \Delta H_f^\circ\end{pmatrix} - \begin{pmatrix}\text{Observed value}\\ \text{of } \Delta H_f^\circ\end{pmatrix}$

$$= 170 - 82 = \mathbf{88 \text{ kJ mol}^{-1}}.$$

Example 4.22. *Both methane and ethane can be used as fuels. If the values of ΔH_f° for $CH_4(g)$, $C_2H_6(g)$, $CO_2(g)$ and $H_2O(l)$ are respectively – 74.85, – 84.68, – 393.5 and – 286 kJ mol^{-1}. Predict which of them is a more efficient fuel.*

Solution. A fuel which produces more amount of heat per gram of its combustion is relatively more efficient.

Calculation of enthalpy of combustion of CH_4 and C_2H_6.

Combustion of *Methane* can be represented as :

$$CH_4(g) + 2O_2(g) \longrightarrow CO_2(g) + 2H_2O(l)$$

$$\Delta H_1 = \Sigma\Delta H_f(\textit{products}) - \Sigma\Delta H_f(\textit{reactants})$$

$$= [2(-286) + (-393.5)] - [-74.84]$$

$$= \mathbf{-890.66 \text{ kJ mol}^{-1}}$$

Combustion of ethane is represented as

$$C_2H_6(g) + \frac{7}{2}O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$$

$$\Delta H_2 = [3 \times \Delta H_f(H_2O) + 2\Delta H_f(CO_2)] - \left[\Delta H_f(C_2H_6) + \frac{7}{2} \times 0\right]$$

$$= [3 \times (-286) + 2(-393.5) - [-84.68] = \mathbf{-1560.32 \text{ kJ}}$$

Now, heat evolved per gram of CH_4 $= \dfrac{890.66}{16} = 55.66 \text{ g}^{-1}$

Heat evolved per gram of C_2H_6 $= \dfrac{1560.32}{30} = 52.01$ kJ g

Thus, methane is more efficient fuel.

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MISCELLANEOUS PROBLEMS

4.38. Calculate heat of formation of $C_2H_5OH(l)$ at constant volume from the following data at 298 K.

(*i*) $C(s) + O_2(g) \longrightarrow CO_2(g)$; $\Delta H = -393.5$ kJ

(*ii*) $H_2(g) + \frac{1}{2}O_2(g) \longrightarrow H_2O(l)$; $\Delta H = -286$ kJ

(*iii*) $C_2H_5OH(l) + 3O_2(g) \longrightarrow 2CO_2(g) + 3H_2O(l)$; $\Delta H = -1365.6$ kJ.

[**Hint.** Find ΔH from the data and apply the relation $\Delta H = \Delta E = \Delta nRT$.]

4.39. The standard heat of formation of $CH_4(g)$, $CO_2(g)$ and $H_2O(g)$ are -76.2, -394.8 and -241.6 kJ mol^{-1} respectively. Calculate the amount of heat evolved by burning 1 m^3 of methane measured under N.T.P.

(***Roorkee Entrance 1990***)

4.40. The standard entropies of $CO_2(g)$, $CO(g)$ and $O_2(g)$ are 213.6, 197.7 and 204.82 JK^{-1} mol^{-1} respectively. Calculate the value of $\Delta G°$ for the reaction, $CO(g) + \frac{1}{2}O_2(g) \longrightarrow CO_2(g)$

The value of standard enthalpies of $CO(g)$ and $CO_2(g)$ are -110.94 and -393.3 kJ mol^{-1} respectively.

4.41. For a hypothetical reaction $nX \rightarrow mP$ the value of $\Delta H = -113$ kJ and $\Delta S = -145$ JK^{-1}. Calculate

(*i*) The value of ΔG at 700 K

(*ii*) Value of ΔS_{surr} and $\Delta S_{univ.}$

4.42. Rhombic and monoclinic sulphur are at equilibrium at 95.5°C. The enthalpy change for $S_{(R)} \rightarrow S_{(M)}$ is + 358.8 J. Calculate

(*i*) Entropy change of process

(*ii*) Which form is more stable at 100°C and at 80°C.

4.43. The solubility product of AgCl at 298 K is 1.8×10^{-10}. Calculate the value of $\Delta G°$ for the process

$$AgCl \underset{}{\overset{aq.}{\rightleftharpoons}} Ag^+(aq) + Cl^-(aq).$$

Can we have a solution in which molarity of Ag^+ and Cl^- ion in 1 M.

4.44. 150 Joules of heat flows out of a large reservior of water containing 500 kg of water at 35°C into surroundings at 25°C. Assuming no change in temperature calculate (*i*) ΔS_{sys}. (*ii*) ΔS_{surr}. (*iii*) ΔS_{total}.

4.45. On an average, a person requires 2870 kcal of energy for leading a normal life. How many grams of cane sugar ($C_{12}H_{22}O_{11}$) must be consumed if all the required energy has to be derived from cane sugar. The heats of formation of $C_{12}H_{22}O_{11}(s)$, $CO_2(g)$ and $H_2O(l)$ are given as -530.3, -94 and -68.3 kcal mol^{-1} respectively.

4.46. Calculate free energy change when one mole of sodium chloride is dissolved in water at 25°C. Lattice energy = 777.8 kJ mol^{-1} ; ΔS at 25°C = 0.043 kJ mol^{-1}. Hydration energy for NaCl = -774.1 kJ mol^{-1}. (***CBSE 1993 C***)

SOME IMPORTANT TERMS CONCEPTS AND FORMULAE

- **Thermodynamics.** The branch of science which deals with quantitative relationship between heat and other forms of energies.
- **System.** Part of the universe selected for investigations.
- **Surroundings.** Part of the universe other than the system.
- **Extensive Properties.** Properties of the system which depend upon the quantity of matter contained in it.
- **Intensive Properties.** Properties of the system which are independent of the quantity of matter.

13B

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- **State of System.** The conditions of existence of system when its macroscopic properties have definite values.
- **State Functions.** The thermodynamic quantities which depend only on initial and final state but are independent of the path.
- **Reversible process.** The process which is carried out infinitessimally slowly in such a manner that the system remains almost in the state of equilibrium at every stage.
- **Internal Energy (E).** It is the energy possessed by all the constituent particles of the system at particular conditions of temperature and pressure.
- **Enthalpy (H).** It is the sum of internal energy and PV-energy of the system at particular conditions.
- **Enthalpy of reaction.** The enthalpy change taking place during the reaction when number of reactants and products are same as indicated by balanced chemical equation.
- **Standard Enthalpy of Formation ($H_f°$).** The enthalpy change accompanying the formation of one mole of a compound from the constituent elements at the standard state.
- **Hess's Law.** The enthalpy change in a chemical or a physical process is same whether the process is carried out in one or in several steps.
- **Bond Energy.** The average amount of energy required to break one mole of the bonds of particular type in gaseous molecules.
- **Spontaneous Process.** A process which has an urge or a natural tendency to occur in a particular direction either of its own or after proper initiation under a given set of conditions.
- **Entropy (S).** A thermodynamic quantity, the change in the value of which during the process is given by the ratio of heat absorbed in a reversible manner to the temperature at which it is absorbed.
- **Free-Energy (G).** The amount of energy available from the system under particular set of conditions that can be converted into useful work.
- **First Law of Thermodyamic.** The energy of universe is always conserved during any physical or chemical process.
- **Second Law of Thermodynamics.** The entropy of universe always tends to increase during any spontaneous process.
- **Third Law of Thermodynamics.** At absolute zero, the entropy of a perfectly crystalline substance is zero.

SOME IMPORTANT FORMULAE

- $\Delta E = q + \omega$ or $\Delta E = q - P\Delta V$
- $\Delta H = \Delta E + P\Delta V$ or $\Delta H = \Delta E + \Delta nRT$
- $\Delta H = \Sigma H_f° \text{ (Products)} - \Sigma \Delta H_f° \text{ (Reactants)}$
- $\Delta H = \left[\begin{array}{c}\text{Total energy required}\\ \text{to break the bonds}\end{array}\right] - \left[\begin{array}{c}\text{Total energy given out}\\ \text{in forming bonds}\end{array}\right]$
- $\Delta S = \frac{q_{(rev)}}{T}$; $\Delta S_{vap} = \frac{\Delta H_{vap}}{T_b}$; $\Delta S_{fus.} \frac{\Delta H_{fus}}{T_f}$
- **For process to be spontaneous,** $\Delta S_{Sys} + \Delta S_{Surr} > 0$
- $G = H - TS$ or $G = E + PV - TS$
- $\Delta G = \Delta H - T\Delta S$
- $\Delta G_{sys} = -T\Delta S_{Total}$
- $\Delta G° = \Sigma\Delta G_f° \text{ (Products)} - \Sigma G_f° \text{ (Reactants)}$
- $\Delta G_{T,P} = W_{net}$
- $\Delta G_{T,P} < 0$ refer to spontaneous process
- $\Delta G_{T,P} = 0$ refer to equilibrium conditions.

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EXERCISE

VERY SHORT ANSWER QUESTIONS
(1 Mark)

1. Give an example for each of the following.
   (*i*) Isolated system, (*i*) Open system, (*iii*) Closed system.
2. Comment on the statement that ratio of two extensive properties is intensive in nature.
3. Which out of the following is an intensive property ? Temperature, mass, heat capacity, enthalpy.
4. Out of E, H, *q*, *w* which are state functions.
5. Four coins are placed in a box and the box is shaken vigorously. Which arrangement of coins has the least probability after shaking ?
6. Given that ΔH_f° of Cl(*g*) as 29.0 kcal mol^{-1}, what is the bond dissociation energy of Cl_2 molecule ?
7. A chemical reaction is carried out at two different temperatures T_1 and T_2. Will ΔH of the reaction be same or different.
8. (*i*) Is there any change in entropy during reversible adiabatic process ?
   (*ii*) Is there any change in enthalpy during cyclic process ?
9. Make necessary corrections in following relations
   (*i*) $\Delta S = q/T$, (*ii*) $E = H—TS$, (*iii*) $\Delta G_{T,V} < 0$.
10. At what temperature the entropy of a perfectly crystalline substance is zero.
11. Should the following reaction be favourable at high temperature or at low temperature ?
$$SO_2(g) + \frac{1}{2}O_2(g) \longrightarrow SO_3(g).$$
12. What is free energy of the system ? In what respect does it differ from enthalpy ?
13. For a reaction, both ΔH and ΔS are positive, under what conditions will the reaction occur spontaneously ?
14. Give the relation between $\Delta S_{universe}$ and ΔG.
15. How is free energy change related to entropy change of the process ?
16. Will melting of ice be spontaneous below 273 K at one atmospheric pressure ?
17. Out of, 2 mol O_2 at 100°C, 1 atm and 2 mol of O_2 at 100°C, 10 atm pressure which one has higher entropy ?
18. Give a chemical reaction in which ΔH and ΔE are equal.
19. Differentiate between ΔH° and ΔH_f°.
20. How is free energy related to enthalpy and entropy of the substance ? **(*CBSE 1992*)**
21. Give the relationship between free energy and equilibrium constant.
22. What is the effect of temperature on free energy ?

DESCRIPTIVE QUESTIONS
(2-3 Marks)

Basic Concepts

23. Explain the following terms giving examples :
   (*i*) System (*ii*) Surroundings
   (*iii*) Internal energy (*iv*) Enthalpy.

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24. Classify the following into different types of systems
(*i*) a tea placed in a cup (*ii*) a sealed bottle of soda water in referigerator
(*iii*) a boiling tea placed in thermos flask.

25. What is meant by the following :
(*i*) Thermodynamic process (*ii*) Reversible process
(*iii*) State of the system (*iv*) State functions.

26. Give example to show that ΔE is a state function while q and w are path function.

27. Define intensive and extensive properties. Give suitable examples.

28. What is the difference between *heat energy* and work energy ?

29. Derive the expression for the pressure-volume work.

First Law of Thermodynamics

30. State and explain the first law of thermodynamics. Derive its mathematical form.
(Haryana Board 1992 ; H.P. 1994)

31. Is there a conservation of energy when a ball of mud drops from a height h to ground. If so what happens to its P.E.

32. What is the basic difference between the terms *heat of reaction* and *heat of formation*. Illustrate with examples.

33. State whether each of the following will increase or decrease the total energy content of the system :
(*i*) Heat transferred to surroundings (*ii*) Work done on the system
(*iii*) Work done by the system.

34. What is the necessity of introducing the thermodynamic function *enthalpy* (**H**) ?

35. What do you understand by the notations ΔH and ΔE ? What do they signify ?

36. Derive the relationship between ΔH and ΔE. Point out examples when :
(*i*) $\Delta H = \Delta E$; (*ii*) $\Delta H > \Delta E$; and (*iii*) $\Delta H < \Delta E$.

37. Point out the limitations of first law of thermodynamics.

Second Law of Thermodynamics ; Entropy

38. What is the necessity of introducing second law of thermodynamics ? Explain with examples.

39. What do you understand by the spontaneous process ? Is melting of ice spontaneous at 270 K and 1 atmosphere pressure ?

40. Can ΔH be taken as a sole criterion of the spontaneity of a process ? Justify your answer.

41. Comment on the statement that energy of the universe is constant but entropy of the universe is always increasing.

42. (*i*) What is meant by the term entropy ? Discuss the effect of increased temperature on the entropy of a substance.
(CBSE 1993)
(*ii*) What is the physical significance of entropy ?

43. Give examples to arrive at the conclusions $\Delta S_{Total} > 0$ for spontaneous processes.

44. Based on the relationship of entropy to the degree of disorder in a system, indicate whether the following changes represent an increase or decrease in the entropy of the system :
(*a*) The freezing of water
(*b*) The burning of rocket fuel
(*c*) The sublimation of dry ice
(*d*) The decomposition of ammonium nitrate according to the following equation

$$2NH_4NO_3(s) \longrightarrow 2N_2(g) + 4H_2O(g) + O_2(g).$$

45. Will entropy increase or decrease in the following changes ? Give reasons for your answer.
(*i*) Dissolution of sugar in water (*ii*) Boiling of an egg.

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46. Predict the sign of ΔS (*positive* or *negative*) for the following changes :

(*i*) Stretched rubber band $\longrightarrow$ Loose rubber band

(*ii*) $H_2O(l) \longrightarrow H_2O(s)$ (*iii*) Steam $\longrightarrow$ Water

(*iv*) $Cr^{3+}(aq) + 6H_2O(l) \longrightarrow Cr(H_2O_6)^{2+}(aq)$ (*v*) $CO_2 + H_2O \xrightarrow[\text{Photosynthesis}]{\text{light}}$ carbohydrates + O_2.

47. (*i*) What is entropy criterion ? What are its limitations ?

(*ii*) What are the thermodynamic conditions for the feasibility of the chemical process :

(*a*) at constant T and P (*b*) at constant S and T.

48. Can we predict the spontaneity of a process in closed system from the value of ΔS_{syst} ? Justify your answer.

49. Which of the following terms has no relation with the first law of thermodynamics ?

(*i*) work (*ii*) heat (*iii*) internal energy

(*iv*) entropy (*v*) enthalpy.

Free Energy and Criterion of Spontaniety

50. What is free energy of a system ? Give two of its important characteristics.

51. What is meant by the term *free energy* ? What is the necessity of introducing such a function. (***Har. Board 1992***)

52. What is meant by the notations ΔG, ΔS and ΔH ? What do they signify ? Give relationship between them.

53. Write Gibb's-Helmholtz equation which relates the enthalpy change and free energy change of a process occurring at constant temperature and pressure. How does the equation help in developing the conditions under which ΔG is – ve ?

54. For a process, $\underset{\text{(ice)}}{H_2O(s)} \rightleftharpoons \underset{\text{(water)}}{H_2O(l)}$ at 273 K which of the following is correct and why ?

(*a*) $G_{(ice)} = G_{(water)} = 0$ (*b*) $G_{(ice)} = G_{(water)} \neq 0$

(*c*) $G_{(ice)} > G_{(water)}$ (*d*) $G_{(ice)} < G_{(water)}$.

55. (*a*) Explain the terms *entropy* and *enthalpy*.

(*b*) For a reaction both ΔH and ΔS are positive. Under what conditions the reaction occurs spontaneously ?

56. Although ΔH for the dissolution of NaCl in water + 1.28 kcal/mol yet it is soluble in water, why ?

57. Discuss the role of temperature in determining the spontaneity of a process.

58. Derive the following relations :

(*i*) $T\Delta S_{Total} = -\Delta G$ (*ii*) $-\Delta G_{T,P}$ = useful work.

59. Why endothermic reactions are more probable at high temperature ?

Third Law of Thermodynamics

60. State and explain the third law of thermodynamics.

61. Name and state the laws which :

(*i*) introduces the concept of entropy (*ii*) helps in calculation of entropy.

62. Give the relationship between ΔS and the heat capacity of the substance. What is the importance of this relationship ?

MISCELLANEOUS QUESTIONS

63. Point out the difference if any between :

(*i*) heat and work (*ii*) enthalpy change and internal energy change

(*iii*) ΔS_{Total} and ΔG_{System}.

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64. Account for the following :

(*i*) A real crystal has more entropy than ideal crystal.

(*ii*) Entropy of hexagonal closed packed structure is less than body centred cubic close packed structure.

65. When ammonium chloride is dissolved in water, the solution becomes colder. Can you draw any conclusion regarding enthalpy change, free energy change end entropy change of the process ?

66. Give combined statement of first and second law of thermodynamics. Using the statement together with G = H—TS. Prove that $\Delta G = w_{useful}$.

67. Define the term free energy. Discuss the effect of temperature on free energy change for exothermic reactions. *(Pb. 1992)*

68. Distinguish between the terms *bond energy* and *bond dissociation energy*.

69. Define Enthalpy. Show that change in enthalpy at constant pressure for a reaction involving gases is given by the expression $\Delta H = \Delta E + \Delta n_g RT$. *[H.P. (Sc.) 1993 ; A.I. CBSE (O) 1992]*

70. In any reversible process, $\Delta S_{universe} = 0$ but in irreversible process $\Delta S_{universe} > 0$. Justify.

71. What are spontaneous processes ? Mention conditions for a reaction to be spontaneous at constant temperature and pressure. *(CBSE 1995)*

72. What is free energy and free energy change ? Show that change in free energy is equal to useful work done. *(Pb. Board 1995)*

73. State third law of thermodynamic, and define isolated system. *(CBSE 1995)*

NUMERICAL PROBLEMS

74. Water gas is fuel made by passing steam over red hot coke as $H_2O(g) + C(s) \rightarrow CO(g) + H_2(g)$. Given that ΔH_f° of $H_2O(g)$, $CO(g)$, as – 241.8 and – 110.5 kJ mol^{-1}. Also, the values of S° for $H_2O(g)$, $C(s)$, $CO(g)$ and $H_2(g)$ as 188.7, 197.9, 131.0 and 5.69 JK^{-1} mol^{-1} respectively. Assuming ΔH° and ΔS° to be temperature independent, calculate the temperature at which the reaction becomes favourable.

75. The polymerisation of ethylene to linear polyethylene is represented by reaction

$$nCH_2 = CH_2 \longrightarrow (CH_2 - CH_2)_n$$

where *n* has a large integral value. Given that $\Delta H_{C=C}$ and ΔH_{C-C} at 298 K as + 590 and + 331 kJ mol^{-1}. Calculate enthalpy of polymerisation per mol of ethylene. *(I.I.T. 1994)*

76. A gas expands from a volume of 3.0 dm^3 against a constant external pressure of 3 atm. to a volume of 5.0 dm^3. The work of expansion is used to heat 10 ml of water at 290 K. Calculate the final temperature of the water. *(Roorkee 1993)*

77. 0.16 g of methane was subjected to combustion at 27°C in a bomb calorimeter. The temperature of calorimeter system including water was found to rise by 0.5°C. Calculate heat of combustion of methane at (*i*) constant volume and (*ii*) at constant pressure. (Thermal capacity of calorimeter system is 17.7 kJ K^{-1} and R = 8.31 JK^{-1} mol^{-1}). *(Roorkee 1994)*

78. Calculate the value of equilibrium constant for a reaction at 400 K.

$$2NOCl(g) \rightleftharpoons 2NO(g) + Cl(g)$$

ΔS and ΔH are 122 JK^{-1} mol^{-1} and 77.2 kJ mol^{-1} respectively. *(CBSE 1994)*

79. Calculate ΔG and ΔG° for the process $X + y \rightleftharpoons p + Q$ at 27°C given that value of K is 10^2.

80. Calculate the maximum work that can be obtained when an ideal gas expands isothermally and reversibly at 27°C from the volume of 1.5 L to 2.5 L.

81. At 300 K, the standard enthalpies of formation of $C_6H_5COOH(s)$, $CO_2(g)$ and $H_2O(l)$ are – 408, – 393 and – 286 kJ mol^{-1} respectively. Calculate the heat of combustion of benzoic acid at constant volume and at constant pressure (R = 8.31 JK^{-1} mol^{-1}). *(Roorkee 1995)*

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82. Calculate the standard internal energy change for the following reaction at 25°C

$$2H_2O_2(l) \rightarrow 2H_2O(l) + O_2(g)$$

ΔH_f° of $H_2O_2(l)$ and $H_2O(l)$ are -188.0 kJ mol^{-1} and -286.0 kJ mol^{-1} respectively. ***(CBSE 1995)***

83. Enthalpy change involved in the oxidation of glucose is -2880 kJ mol^{-1}. Twenty five per cent of this energy is available for muscular work. If 100 KJ of muscular work is required to walk one kilometer, what is the maximum distance that a person will be able to walk after eating 120 g of glucose. ***(I.I.T. 1997)***

84. Compute the heat of formation of liquid methanol in kilo Joules per mole, using the following data. Heat of vapouration of liquid methyl alcohol = -38 kJ mol^{-1}. Also ΔH_f° of $H(g)$, $C(g)$ and $O(g)$ respectively are 218, 715 and 247 kJ mol^{-1}. Also ΔH_{C-H}, ΔH_{C-O}, ΔH_{O-H} being 415, 356, 463 kJ mol^{-1} respectively. ***(I.I.T. 1997)***

85. Anhydrous $AlCl_3$ is covalent. Form the data given below predict whether it would remain covalent or become ionic in aqueous solution IE of Al = 5137 kJ mol^{-1}. $\Delta H_{Hydration}$ of Al^{3+} = -4665 kJ mol^{-1} ; $\Delta H_{hydration}$ of Cl^- = -381 kJ mol^{-1}. ***(I.I.T. 1997)***

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FOR THE COMPETITIVE EXAMS

MULTIPLE CHOICE QUESTIONS

Select the correct answer from each of the following questions :

1. For an exothermic reaction, which of the following is always < 0

(*a*) ΔS (*b*) ΔT (*c*) ΔH (*d*) none of these.

2. The relationship between ΔG and ΔS is

(*a*) $\Delta G = \Delta S + T\Delta H$ (*b*) $\Delta S = \Delta G - T\Delta H$ (*c*) $\Delta H = \frac{\Delta S - \Delta G}{T}$ (*d*) $\Delta S = \frac{\Delta H - \Delta G}{T}$.

3. When a solid melts, there is

(*a*) an increase in enthalpy (*b*) no change in enthalpy

(*c*) a decrease in enthalpy (*d*) a decrease in internal energy.

4. Which of the following is the least random state of H_2O ?

(*a*) Ice (*b*) Liquid Water

(*c*) Steam (*d*) All represent same random state.

5. Which one of the following processes is not spontaneous

(*a*) dissolution of copper sulphate in water (*b*) reaction between hydrogen and oxygen to form water

(*c*) water flowing downhill (*d*) flow of current from low potential to high potential.

6. Which of the following relations is not correct ?

(*a*) $\Delta H = \Delta E - P\Delta V$ (*b*) $\Delta E = q + W$ (*c*) $\Delta S_{syst} + \Delta S_{surr} \geq 0$ (*d*) $\Delta S_{fusion} = \frac{\Delta H_{fusion}}{T}$.

7. A minus sign of the free energy change denotes that

(*a*) the reaction tends to proceed spontaneously (*b*) the reaction is non-spontaneous

(*c*) the system is in equilibrium (*d*) the reaction is exothermic.

8. The absolute entropy of a free element is

(*a*) always negative (*b*) always zero (*c*) always positive (*d*) zero at 273 K.

9. The concept of entropy was introduced by

(*a*) First law of thermodynamics (*b*) Second law of thermodynamics

(*c*) Third law of thermodynamics (*d*) None of the above.

10. Which of the following is zero during adiabatic expansion of the gas

(*a*) ΔT (*b*) ΔS (*c*) ΔE (*d*) None of these.

11. For a reversible process at equilibrium, the entropy change ΔS is given by

(*a*) $\Delta H/\Delta T$ (*b*) $T/q_{(rev)}$ (*c*) $\frac{q_{(rev)}}{T}$ (*d*) $T\Delta H$.

12. Which of the following is not a characteristic of entropy ?

(*a*) It is a state function (*b*) It is macroscopic property

(*c*) It is extensive property (*d*) It is intensive property.

13. The relationship between equilibrium constant K and free energy change of the process is given by

(*a*) $\Delta G = -RT \log K$ (*b*) $\Delta G^\circ = RT \log 1/K$

(*c*) $\Delta G^\circ = 2\ RT \log K$ (*d*) $\Delta G^\circ = 2.303\ RT \log K^{-1}$

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14. Which name is associated with the relation, $\Delta G = \Delta H - T\Delta S$
(a) Maxwell (b) Gibb's Helmholtz (c) Trounton (d) Boltzmann.

15. For which of the following process ΔS_{Total} is < 0
(a) Intermixing of gases (b) Melting of ice below – 4°C at 1 atm pressure
(c) Evaporation of water above 100°C (d) Burning of hydrogen in oxygen.

16. A process is spontaneous at all temperatures, if
(a) $\Delta H < 0$; $\Delta S < 0$ (b) $\Delta H < 0$; $\Delta S > 0$ (c) $\Delta H = 0$; $\Delta S < 0$ (d) $\Delta H > 0$; $\Delta S < 0$.

17. "*The entropy of a perfect crystal at absolute zero is zero.*" The statement corresponds to which law of thermodynamics
(a) Zeroth law (b) Second law (c) Third law (d) First as well as Second.

18. What is correct about the expression – $P\Delta V$?
(a) It refers to work of expansion only (b) It refers to work of contraction only
(c) It refers to all type of pressure-volume work, in general
(d) None is correct.

19. For a natural process in any isolated system
(a) $\Delta S > 0$ (b) $\Delta S > 0$ (c) $\Delta S \geq 0$ (d) $\Delta S \leq 0$.

20. The energy change of reaction is $C_2H_6(g) \rightarrow 2C(g) + 6H(g)$ is x kJ. The bond energy of C—H bond is
(a) $\frac{x}{6}$ kJ (b) $\frac{x}{3}$ kJ
(c) x kJ (d) data is insufficient to predict it.

21. Which of the following is not a state property ?
(a) E (b) H (c) T (d) Dipole moment.

22. If a system absorbs reversibly 600 J of heat and performs 250 J of work, the increase in the internal energy of the system is
(a) 850 J (b) 350 J (c) 250 J (d) 600 J.

23. Which of the following quantity is not a state function ?
(a) Temperature (b) Entropy (c) Enthalpy (d) Work.

24. The enthalpy of formation of Cl(g) is x kJ mol^{-1}. The value of $\Delta H_{Cl—Cl}$ will be
(a) x kJ mol^{-1} (b) $2x$ kJ mol^{-1} (c) $\frac{x}{2}$ kJ mol^{-1} (d) unpredictable.

25. For a process at equilibrium
(a) $\Delta S_{total} > 0$ (b) $\Delta H_{sys} = 0$ (c) $\Delta G_{T,P} < 0$ (d) $\Delta S_{total} = 0$.

26. The standard enthalpies of formation of $NO_2(g)$ and $N_2O_4(g)$ are 8 and 2 kcal mol^{-1} respectively. The heat of dimerisation of NO_2 in gaseous state is
(a) 10 kcal mol^{-1} (b) 6.0 kcal mol^{-1} (c) – 14 kcal mol^{-1} (d) – 6.0 kcal mol^{-1}.

27. Which of the following process is endothermic ?
(a) C (graphite) → C (diamond) (b) $C(s) + O_2(g) \rightarrow CO_2(g)$
(c) Combustion of carbon monoxide (d) $Cl(g) \rightarrow Cl^-(g)$.

28. Which of the following substance has zero value of ΔG_f° ?
(a) $Br_2(aq)$ (b) $Br_2(l)$ (c) Br(g) (d) $Br_2(s)$.

29. Which parameter always increases during spontaneous change ?
(a) ΔG (b) ΔS_{Total} (c) ΔH (d) $\Delta n(g)$.

30. The bond energy of O—H bond is 109 kcal mol^{-1}. The value of ΔH_f of $H_2O(g)$ is
(a) – 218 kcal mol^{-1} (b) 109 kcal mol^{-1} (c) unpredictable from the data (d) + 218 kcal mol^{-1}.

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31. Molar heat capacity of water in equilibrium with ice at constant pressure is
(*a*) zero (*b*) ∞ (*c*) 40.45 kJ K^{-1} mol^{-1} (*d*) 75.48 JK^{-1} mol^{-1}.
(*I.I.T. 1997*)

32. Standard molar enthalpy of formation of CO_2 is equal to
(*a*) zero
(*b*) Standard molar enthalpy of combustion of gaseous carbon
(*c*) Standard molar enthalpy of combustion of carbon (graphite)
(*d*) sum of molar enthalpies of formation of CO and O_2. (*I.I.T. 1997*)

33. Given that, $C + O_2 \longrightarrow CO_2$; $\Delta H° = -x$ kJ and
$2CO + O_2 \longrightarrow 2CO_2$; $\Delta H° = -y$ kJ.
The standard enthalpy of formation of carbon moxide is
(*a*) $y - 2x$ (*b*) $\frac{2x - y}{2}$ (*c*) $\frac{y - 2x}{2}$ (*d*) $2x - y$.
(*CBSE, Med. 1997*)

ASSERTION-REASON TYPE QUESTIONS

In the following questions, two statements are given ; One labbled as ***Assertion* A** and the other as ***Reason* R.** Examine the two statements carefully and mark the correct choice (*a*), (*b*), (*c*) or (*d*) according to the instructions given below.

(*a*) If both **A** and **R** are correct and **R** is correct explanation of **A**
(*b*) If both **A** and **R** are correct but **R** is not the explanation of **A**
(*c*) If **A** is correct but **R** is wrong
(*d*) If **A** is wrong but **R** is correct.

34. ***Assertion* A :** Reversible process and cyclic process have same meaning.
***Reason* R :** ΔH_{cycle} and ΔE_{cycle} is zero.
(*a*) (*b*) (*c*) (*d*)

35. ***Assertion* A :** No heat engine has efficiency of 100%.
***Reason* R :** Complete conversion of heat into work is not possible.
(*a*) (*b*) (*c*) (*d*)

36. ***Assertion* A :** For the process to be spontaneous ΔG as well as ΔS has to be less than zero.
***Reason* R :** For spontaneous change, $\Delta S_{Total} > 0$.
(*a*) (*b*) (*c*) (*d*)

37. ***Assertion* A :** Absolute values of H and E cannot be determined .
***Reason* R :** Both H and E are State functions.
(*a*) (*b*) (*c*) (*d*)

38. ***Assertion* A :** Mass and volume are extensive properties.
***Reason* R :** Mass/volume is also extensive parameter.
(*a*) (*b*) (*c*) (*d*)

39. ***Assertion* A :** ΔH of a reaction is independent of temperature.
***Reason* R :** ΔH° of a reaction = ΣH° (Products) – ΣH° (Reactants).
(*a*) (*b*) (*c*) (*d*)

40. ***Assertion* A :** ΔG and ΔH of a reaction always have same sign.
***Reason* R :** $\Delta G_f°$ of carbon (graphite) is equal to zero.
(*a*) (*b*) (*c*) (*d*)

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FILL IN THE BLANKS

Fill in the blanks in each of the following questions with appropriate items :

1. On changing temperature, the value of ΔH of reaction .....
2. For spontaneous reaction, the value of ΔG must be less than .....
3. There is greater disorder in the liquid state as compared to the .....
4. A property of substances called ..... measures the randomness in them.
5. The overall factor which determines whether or not a reaction is feasible is the .....
6. The ..... work is also called useful work.
7. A reaction will proceed spontaneously if the reactants have ..... energy as compared to products.
8. Law of conservation of energy is also known as .....
9. If ΔG is ..... the reaction does not proceed in the forward direction.
10. Gibbs-Helmholtz equation is $\Delta G = \Delta H$ .....
11. By definition heat content of the system is given by the expression .....
12. The internal energy of ideal gas depends only on its .....
13. The heat absorbed in a isothermal and isobaric process is equal to .....
14. The mathematical expression for first law of thermodynamics is .....
15. The expression leading to the statement of second law of thermodynamics in terms of entropy is .....
16. Enthalpy is an ..... property *(I.I.T. 1997)*
17. When Fe(s) is dissolved is aqueous hydrochloric acid in a closed vessel the work is ..... *(I.I.T. 1997)*

TRUE/FALSE STATEMENTS

Select the true and false statement out of the following :

1. Spontaneous reactions never require initiation.
2. Negative value of ΔS is the sole criterion of spontaneity.
3. Second law of thermodynamics tells that entropy of universe is constant.
4. The dissociation of ammonium chloride involves an increase in randomness.
5. $\Delta S = \frac{w}{T}$.
6. For combustion of carbon monoxide, the value of ΔH is less than ΔE.
7. Melting of ice involves a decrease in randomness and increase in enthalpy.
8. A spontaneous process left of itself ultimately attains a state of equilibrium.
9. Like enthalpy and internal energy, the absolute value of standard entropy for elementry substances is zero.
10. In general exothermic reactions are favourable at low temperature.
11. In isothermal process, $\Delta T = 0$ because no heat enters or leaves the system.
12. ΔH = heat change taking place during the reaction at constant T and constant volume.
13. Free energy is property of the system which measures its randomness.
14. The entropy of real crystal is more than the entropy of ideal crystal.
15. The larger the – ve value of ΔH_f°, stabler will be the compound with respect to its constituent elements.

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MATCHING TYPE QUESTION

Match the entries of column A with appropriate entries of column B and column C :

Column A	Column B	Column C
1. Adiabatic process	1. Measure of disorder in the system	1. Work done is maximum under these conditions
2. Reversible process	2. $\Delta S_{Total} > 0$	2. May or may not be spontaneous
3. Spontaneous process	3. $\Sigma\Delta G_f^\circ(P) - \Sigma\Delta G_f^\circ(R)$	3. The process occurs in isolated systems
4. Exothermic reaction	4. $\delta q = 0$	4. $\Delta G_{T,P} < 0$
5. ΔS_{System}	5. $\Delta H < 0$	5. $\Delta H^\circ - 298\ \Delta S^\circ$
6. ΔG°	6. A processes which is carried out infinitessimally slowly under equilibrium conditions	6. $\frac{\delta q_{(rev)}}{T}$

ANSWERS/HINTS

REVIEW PROBLEMS

4.1. – 17.99 J **4.2.** $(E_1 + 150)$ J **4.3.** 160 J

4.4. – 887.47 kJ **4.5.** – 3264 kJ mol^{-1} [**Hint.** $\Delta E = 41.80 \times 78 = -3260.40$ kJ, $\Delta n = -3/2$]

4.6. 114.74 kJ **4.7.** – 329.52 kJ **4.8.** – 890.7 kJ

4.9. – 3169.96 kJ **4.10.** $\Delta H^\circ = 13.13$ kJ ; $\Delta E^\circ = 128.8$ kJ

4.11. – 1367.3 kJ mol^{-1} **4.12.** 345.7 kJ **4.13.** – 125 kJ

4.14. 390.66 kJ mol^{-1} **4.15.** – 88.8 kJ **4.16.** 713.98 kJ mol^{-1}

4.17. 88.3 JK^{-1} mol^{-1} **4.18.** 84.87 JK^{-1} mol^{-1} **4.19.** 22.06 JK^{-1} mol^{-1}

4.20. 156.4 K **4.21.** 527.53 J **4.22.** 1035.7 K

4.23. 121.61 JK^{-1} mol^{-1} **4.24.** 373.4 K **4.25.** Feasible

4.26. – 0.568 kJ mol^{-1} **4.27.** $\Delta G = 0$ at 463 K, non-spontaneous below 463 K

4.28. (*a*) spontaneous ; (*b*) non-spontaneous **4.29.** Above 282.4 K

4.30. – 1010.8 kJ **4.31.** – 141.8 kJ **4.32.** 1.96×10^{-4}

4.33. 38.47 kJ mol^{-1} **4.34.** – 33.8 JK^{-1} **4.35.** – 3.435 kJ

4.36. (*a*) – 242.8 JK^{-1} (*b*) 214.5 JK^{-1} **4.37.** – 94.8 JK^{-1}

4.38. – 270.73 kJ [**Hint.** Find ΔH and apply the relation, $\Delta H = \Delta E + \Delta nRT$]

4.39. 3.579×10^4 J **4.40.** $\Delta G^\circ = -256.57$ kJ

4.41. $\Delta G = -11.5$ kJ mol^{-1} ; $\Delta S_{surr} = -161.42$ JK^{-1} ; $\Delta S_{univ.} = +16.43$ JK^{-1}

4.42 (*i*) $\Delta S = 0.96$ JK^{-1} (*ii*) monoclinic at 100°C and rhombic at 80°C

4.43. $\Delta G = 55.86$ kJ mol^{-1} ; No, such a solution is not possible

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4.44. (*i*) $-0.487\ JK^{-1}$ (*ii*) $0.5033\ JK^{-1}$ (*iii*) $+0.0163\ JK^{-1}$

4.45. 728 g **4.46.** – 9.1 kJ

VERY SHORT ANSWER QUESTIONS

4. E and H. **5.** Four heads or four tails. **6.** 58 kcal mol^{-1}.

7. Different. The two values of ΔH_1 and ΔH_2 are related to each another by Kirchhoff's equation.

$$\frac{\Delta H_2 - \Delta H_1}{T_2 - T_1} = [C_p\,(\text{Products}) - C_p\,(\text{Reactants})]$$

C_p refers to heat capacity at constant pressure.

8. (*i*) No, because $\delta q = 0$ for adiabatic process

(*ii*) No, the system returns to original state after undergoing series of changes.

9. $\Delta S = \frac{q(\text{rev})}{T}$; $G = H - TS$; $\Delta G_{T,P} < 0$.

10. At absolute zero.

11. Low temperature, because it is an exothermic process.

12. Enthalpy is total energy associated with system while free energy is the energy available to be converted into useful work.

G	=	H	–	TS
(Free energy)		(Enthalpy)		(Random Energy)

13. When $T\Delta S > \Delta H$. **14.** $-\Delta G = T\Delta S_{universe}$ **16.** non-spontaneous.

17. At particular temperature, the entropy change is given by

$$\Delta S = 2 \times 2.303\ C_v \log \frac{P_1}{P_2} = 2 \times 2.303\ C_v \log \frac{1}{10} = -4.606\ C_v$$

Thus, entropy of 2 mole of O_2 at 100° and 1 atm pressure is higher.

21. $\Delta G° = -2.303\ RT \log K$.

DESCRIPTIVE QUESTIONS

31. Melting of ice below 273 K is non-spontaneous at 1 atm pressure.

42. In general entropy increases by rise in temperature.

44. (*a*) Decrease of entropy (*b*) Increase in entropy (*c*) Increase in entropy (*d*) Increase in entropy.

45. (*i*) Entropy increases

(*ii*) Entropy increases : During boiling of egg, denaturation of proteins occur due to cleavage of H-bonds. Since denatured proteins have large number of random configurations whereas a normal proteins exist in a particular configurations.

46. (*i*) + ve (*ii*) – ve (*iii*) – ve (*iv*) – ve (*v*) – ve.

61. (*i*) Second law of thermodynamics (*ii*) Third law of thermodynamics.

74. $\Delta H = [-110.5 + 0] - [-241.8 + 0] = 131.3$ kJ

$\Delta S = [197.9 + 131.0] - [189.7 + 5.69] = 134.55\ JK^{-1}$

At equilibrium, $\Delta H = T\Delta S$ or $T = \frac{\Delta H}{\Delta S} = \frac{131.3 \times 10^3}{134.5} = 967$ K

The reaction would be spontaneous above **976 K.**

75. $n(CH_2 = CH_2) \longrightarrow -(-CH_2-CH_2-)_n-$

ΔH (Polymerisation) $= \Delta H_{C=C} - 2 \times \Delta H_{C-C} = 590 - 2 \times 331 = -72$ **kJ mol^{-1}.**

76. $W_{PV} = -P\Delta V = -3\,(5-3) = -6$ L-atm $= -6 \times 101.325 = -607.95$ J

Molar heat capacity of water $= 4.184 \times 18 = 75.312\ JK^{-1}\ mol^{-1}$

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Now $Q = mS\Delta T$ or $\Delta T = Q/mS = \frac{607.95}{10 \times 75.312} = 0.807°$

Final temperature = 290 + 0.807 = **290.807 K.**

77. $\Delta E_{comb.} = -$ **885 kJ mol^{-1}** ; $\Delta H_{comb.} = -$ **889.986 kJ mol^{-1}.**

78. $C_6H_5COOH + \frac{15}{2}O_2 \longrightarrow 7CO_2 + 3H_2O$ ∴ $\Delta n = 7 - 5/2 = -0.5$.

78. $\Delta G° = -2.303\ RT \log K$ or $\log K = -\frac{28400}{2.303 \times 8.314 \times 400} = 4.292$ or $K =$ **1.96×10^{-4}.**

79. $\Delta G° =$ **-11.48 kJ.**

80. Maximum work $= -2.303\ nRT \log \frac{V_2}{V_1}$

$= -2.303 \times 0.75 \times 0.082 \times 300 \log \frac{25}{15} =$ **-9.436 J.**

81. $C_6H_5COOH + \frac{13}{2}O_2 \longrightarrow 7CO_2 + 3H_2O$

$q(p) = \Delta H = 7 \times (-393) + 3(-286) - (-408) - 0$

$= -2571 - 858 + 408 =$ **-3201 kJ mol^{-1}**

$\Delta n = 7 - 13/2 = 0.5$

$q_{(V)} = \Delta E = \Delta H - \Delta nRT = -3201 - 0.5 \times 8.31 \times 10^{-3} \times 300 =$ **-3202.25 kJ mol^{-1}.**

82. $\Delta H =$ **-196 kJ** ; $\Delta E = -198.47$ kJ.

83. $C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O$; $\Delta H = -2880$ kJ mol^{-1}

Energy available from 180 g of glucose for muscular work $= \frac{2880 \times 25}{100} = 720$ kJ

Energy available from 120 g of glucose $= \frac{720 \times 120}{180} = 480$ kJ

Distance travelled from 100 kJ of muscular work = 1 km

Distance travelled from 480 kJ of muscular work $= \frac{480}{100} =$ **4.8. km**

84. $C\,(graphite) + 2H_2(g) + \frac{1}{2}O_2(g) \longrightarrow CH_3OH(g) \longrightarrow CH_3OH(l)$

$\Delta H = [\Delta H_f(C(g)) + 2\Delta H_{H-H} + \frac{1}{2}\Delta H_{O=O}] - [\Delta H_{C-O} + 3\Delta H_{C-H} + \Delta H_{O-H}] - \Delta H_{cond}$

$= [\Delta H_f(C(g)) + 4\Delta H_f(H(g)) + \Delta H_f(O)] - [\Delta H_{C-O} + 3\Delta H_{C-H} + \Delta H_{O-H}] - \Delta H_{Cond}\,(CH_3OH)$

$= (715 + 4 \times 218 + 249) - (356 + 3 \times 415 + 463) - 38 =$ **-266 kJ mol^{-1}.**

85. It will become ionic because energy release by hydralion of Al^{3+} and $6Cl^{-1}$ ions is larger than IE Of Al.

MULTIPLE CHOICE QUESTIONS

1. (*c*)	**2.** (*d*)	**3.** (*a*)	**4.** (*a*)	**5.** (*d*)	**6.** (*a*)
7. (*a*)	**8.** (*c*)	**9.** (*b*)	**10.** (*b*)	**11.** (*c*)	**12.** (*d*)
13. (*d*)	**14.** (*b*)	**15.** (*b*)	**16.** (*b*)	**17.** (*c*)	**18.** (*c*)
19. (*a*)	**20.** (*d*)	**21.** (*d*)	**22.** (*b*)	**23.** (*d*)	**24.** (*b*)
25. (*d*)	**26.** (*c*)	**27.** (*a*)	**28.** (*b*)	**29.** (*b*)	**30.** (*c*)
31. (*b*)	**32.** (*c*)	**33.** (*c*)	**34.** (*d*)	**35.** (*a*)	**36.** (*d*)
37. (*c*)	**38.** (*c*)	**39.** (*d*)	**40.** (*d*).		

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FILL IN THE BLANKS

1. also changes
2. zero
3. solid state
4. entropy
5. free energy change
6. non-PV-work
7. larger free energy
8. first law of thermodynamics
9. positive
10. $-T\Delta S$
11. $H = E + PV$
12. temperature
13. ΔE
14. $\Delta E = q + w$
15. $\Delta S_{Sys} + \Delta S_{Surr} > 0$
16. extensive
17. zero

TRUE/FALSE STATEMENTS

1. False
2. False
3. False
4. True
5. False
6. True
7. False
8. True
9. False
10. True
11. False
12. False
13. False
14. True
15. True.

MATCHING TYPE QUESTIONS

1—3—4 2—6—1 3—2—4 4—5—2 5—1—6 6—3—5.

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5

Electrochemistry

LEARNING OBJECTIVES

- *Electrolytic conduction and the factors affecting conductance ;*
- *Voltaic cells*
- *Electrode potential and electromotive force*
- *Gibb's free energy and cell potential*
- *Electrode potential and electrolysis*
- *Primary cells including fuel cells*
- *Corrosion.*

Electrical energy plays a significant role in our daily life. A large number of industrial porcesses bank upon the use of electrical energy. Many of the chemical transformations are also associated with electrical energy. For example, water decomposes into hydrogen and oxygen gases when electricity is passed through it in the presence of small amount of an acid or a base. Similarly, indirect redox reaction between zinc and copper sulphate results in the liberation of electrical energy. Thus, there is a definite relationship between electrical energy and chemical energy. ***The brance of chemistry which deals with the study of relationship between electrical energy and chemical energy and interconversion of one form into another is called electrochemistry.*** Before we take up the different aspects of electrical energy let us be familiar with some common terms.

5.1. SOME COMMON TERMS

1. Conductors. *The substances which allow the passage of electricity through them* are called **conductors.** On the other hand, the substances which do not allow the passage of electricity through them are called **insulators or non-conductors.** The conductors can be broadly classified into two categories, namely ; *metallic conductors* and *electrolytes.*

(*a*) **Metallic conductors.** These are the *metallic substances which allow the passage of electricity through them without undergoing any chemical change.* Some common examples are copper, silver, aluminium, etc. The conduction through metals is due to the movement of electrons in the metallic crystals.

(*b*) **Electrolytes.** *These are the substances which allow the passage of electricity through their molten state or through their aqueous solutions and also undergo chemical decomposition at the same time.* Some common examples of electrolytes are acids, bases and salts. The conduction through the electrolytes is due to the movement of ions. It is generally referred to as *electrolytic conduction.*

The important points of differences between conduction of electricity through metals and that through electrolytes have been given below in Table 5.1.

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Table 5.1. Comparison of Electrolytic and Metallic Conduction

Metallic Conduction	*Electrolytic Conduction*
1. Conduction through metals is carried by the movement of electrons.	1. Conduction through electrolytes is carried by movement of ions.
2. No change is observed in the chemical properties of the conductors.	2. It involves chemical change resulting in the decomposition of electrolytes.
3. It does not involve any transfer of matter.	3. It involves the transfer of matter as ions.
4. The resistance of metals is due to obstacles of vibrating kernels of metal atoms.	4. The resistance of the solution of electrolyte is due to factors like inter-ionic attraction, viscosity of solvent etc.
5. It shows increase in *resistance* with the increase in temperature.	5. It shows decrease in *resistance* with the increase in temperature.
6. The conductivity of metals is generally high.	6. The conductivity of electrolytic solutions is generally low.

2. Non-electrolytes. The substances which do not conduct electricity either in their molten state or through their aqueous solution are called **non-electrolytes.** Some examples of non-electrolytes are : ethyl alcohol, sugar, glucose, glycerine, etc.

Factors affecting electrolytic conduction

The conduction of electricity through the molten electrolytes or through their aqueous solutions occurs as a result of the movement of the ions. The electrical conductivity of the solutions of electrolytes is, thus, governed by the following factors :

(*i*) **The inter-ionic attraction.** These are the interactions between the ions of the solute and are referred to as *solute-solute interaction.* Larger the interionic attraction, smaller will be the electrical conductivity.

(*ii*) **The solvation of ions.** These are the interactions between the ions of the solute and molecules of the solvent and are referred to as *solute-solute interactions*. Larger the solute-solvent interactions greater is the extent of solvation and lower will be the electrical conductivity of the solution.

(*iii*) **Viscosity of solvent.** This factor depends upon the interactions between the solvent-molecules which is referred to as *solvent-solvent interactions*. Larger the solvent-solvent interactions, larger will be the viscosity and lower will be the electrical conductivity.

(*iv*) **Temperature.** As the temperture of electrolyte solution is increased, the effect of above factors diminishes and kinetic energy of the ions increases. This results in the increase of electrical conductance of electrolytic solutions.

Let us study some basic concepts and terms before we discuss the ability of the electrolytes to conduct electricity.

---

1. Ohm's Law. This law is obeyed by both the metallic as well as electrolytic conductors. It states that *the potential difference across the conductor is directly proportional to the current flowing through it.* That is,

$$\text{Potential difference} \propto \text{Current} \quad \text{or} \quad \frac{\text{Potential difference}}{\text{Current}} = \text{Constant.}$$

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Thus, *ratio of potential difference across the conductor to the current flowing through it is constant.* This constant is called the **resistance** of the conductor. Resistance refers to obstruction to the flow of electricity.

If I is the current strength,

V is the potential difference, and

R is the resistance of the conductor

then according to Ohm's law $\frac{V}{I} = R$ or $I = \frac{V}{R}$

Units. I is expressed in *amperes*, **V** in *volts* and **R** is expressed in *ohms* also designated as Ω.

Resistance (R) of any conductor is the obstruction to the flow of current. It is *directly* proportional to the *length (l)* of the conductor and *inversely* proportional to its *area (a)* of cross-section.

Thus, $R \propto \frac{l}{a}$ or $R = \rho \frac{l}{a}$

where ρ (rho) is the constant of proportionality and is also known as **specific resistance** or **resistivity**. It is given by the expression

$$\rho = R\frac{a}{l}$$

If $l = 1$ cm ; $a = 1$ cm^2, then $R = \rho$

This leads us to define **resistivity** as *the resistance offered by the conductor of 1 cm length with area of cross-section equal* to 1 cm^2. It may also be defined as the resistance offered by a *centimetre cube of a conductor*. The units of specific resistance can be derived from the formula as

$$\rho = R\frac{a}{l} = \text{ohm}\,\frac{\text{cm}^2}{\text{cm}} = \textbf{ohm-cm or } \Omega \textbf{ cm.}$$

2. Conductance. Conductance is a measure of the ease with which current flows through the conductor. It may be defined as the *reciprocal of resistance*. It is denoted by C.

$$C = \frac{1}{R}.$$

Units. The units of conductance are 1/ohm, *i.e.*, Ω^{-1} or **ohm^{-1}** or **mho.**

The electrical conductance is also expressed in *Siemens*, S

$$1\ S = 1\ \Omega^{-1}.$$

3. Specific conductance. *It is the reciprocal of specific resistance* and is also called **conductivity**. It may also be defined as the *conductance of one centimetre cube of the conductor*. It is generally denoted by a Greak letter Kappa (κ).

$$\kappa = \frac{1}{\rho} = \frac{1}{R}\left(\frac{l}{a}\right).$$

Units. The units of conductivity as derived from the above formula are :

$$\kappa = \frac{1}{\rho} = \frac{1}{\text{ohm-cm}} = \textbf{Ohm}^{-1}\ \textbf{cm}^{-1} \text{ or } \Omega^{-1}\ \textbf{cm}^{-1} \text{ or } \textbf{S cm}^{-1}.$$

Note. In *SI units*, area of cross-section is expressed in m^2 and length is expressed in m. Then the units of conductivity will be S m^{-1} or Ω^{-1} m^{-1}.

$$1\ \Omega^{-1}\ \text{cm}^{-1} = 100\ \Omega^{-1}\ \text{m}^{-1}.$$

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The conductivities of some substances are given in Table 5.2.

Table 5.2. Conductivities of Some Substances at 298 K

Substance	$\kappa(ohm^{-1}\ cm^{-1})$	*Substance*	$\kappa(ohm^{-1}\ cm^{-1})$
Pure water	6.0×10^{-5}	Teflon	1×10^{-16}
0.1 M HCl	3.5×10^{-2}	Glass	1×10^{-14}
0.1 M NaCl	9.2×10^{-3}	Graphite	1.2×10^{3}
0.01 M NaCl	1.2×10^{-4}	Iron metal	1.9×10^{5}
0.1 M CH_3COOH	4.7×10^{-4}	Silver metal	5.0×10^{5}
0.01 M CH_3COOH	1.6×10^{-4}		

5.3. EQUIVALENT CONDUCTIVITY OF ELECTROLYTIC SOLUTIONS

The **conductivity** of a metallic conductor has a definite value at a given temperature. However, in case of *electrolytic solution* the conductivity not only depends on temperature but also varies with the concentration of the solution. It is due to the fact that conductivity of a solution is attributed to the presence of ions. The number of ions in one centimetre cube of the solution changes with the variation in concentration. In order to compare the *conductivity* of different electrolytes, it is necessary to consider the solutions of equivalent concentrations, *i.e.*, solutions which are capable of furnishing *ions carrying the same total charge of electricity*. For example, *one gram equivalent* of different electrolytes in the solutions produce ions having same total charge of electricity*. Thus, the most convenient method used to compare the conductivities of electrolytes is to express them as *equivalent conductivity*.

Equivalent conductivity is defined as the *conductance of a solution containing 1 gm-equivalent of electrolyte such that the entire solution is placed between two elecrodes one centimetre apart*. It is denoted by the symbol Λ_{eq}.

Relationship between conductivity (κ) and equivalent conductivity (Λ_{eq}). In order to derive relationship between κ and Λ_{eq} let V cm^3 of the solution containing *1 gm-equivalent* of electrolyte be placed between two large electrodes 1 cm apart.

Let the measured conductance of the solution = x.

As the solution contains 1 gm-equivalent of electrolyte, therefore, the measured conductance also represents the equivalent conductance. Hence, $\Lambda_{eq} = x$.

As the volume of solution is V cm^3.

The number of centimetre cubes in V cm^3 = V

The conductivity (κ) is the conductance of 1 centimetre cube of solution.

$$\therefore \qquad \kappa = \frac{x}{V} \quad \text{or} \quad \kappa = \frac{\Lambda_{eq}}{V} \quad \text{or} \quad \Lambda_{eq} = \kappa V$$

where, V refers to the volume containing 1 gm-equivalent of electrolyte.

*Let us consider same volume of two solutions containing one mole each of NaCl and Na_2SO_4 respectively. One mole of NaCl produces one mole of Na^+ ions and 1 mole of Cl^- ions. On the other hand, one mole of Na_2SO_4 produces 2 moles of Na^+ ions and one mole of SO_4^{2-} ions. It is evident, therefore, that 1 mole of NaCl yields ions carrying 2 faradays of electricity while 1 mole of Na_2SO_4 yields ions carrying 4 faradays of electrolity. But if we take 1 gram-equivalent of NaCl and 1 gm-equivalent of Na_2SO_4 ($\frac{1}{2}$ mole), then each one will produce ions carrying 2 faradays of electricity.

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If C is the concentration of solution in gram-equivalents per litre, *i.e.*, normality of the solution, then the volume of solution containing one gram-equivalent of electrolyte can be calculated as

C gram-equivalents of electrolyte are present in = 1000 cm^3 of solution

1 gram-equivalent of electrolyte is present in = $\frac{1000}{C}$ cm^3 of solution

Thus,
$$\Lambda_{eq} = \frac{\kappa \times 1000}{C} = \frac{\kappa \times 1000}{N}$$

where, N is the normality of the solution.

Units. The units of equivalent conductivity as derived from the formula are

$$\Lambda_{eq} = \frac{\kappa \times 1000}{C} = \frac{ohm^{-1}\ cm^{-1} \times cm^3}{\text{gm-equivalent}}$$

$$= \mathbf{ohm^{-1}\ cm^2\ equivalent^{-1}} \text{ or } \mathbf{\Omega^{-1}\ cm^2\ equivalent^{-1}} \text{ or } \mathbf{S\ cm^2\ equivalent^{-1}}.$$

5.4. MOLAR CONDUCTIVITY

Molar conductivity is defined as the *conductance of the soluiton containing one gram-mole of the electrolyte such that the entire solution is placed between two parallel electrodes one centimetre apart.* It is denoted by Λ_m. Molar conductivity is related to conductivity (κ) by the relation

$$\Lambda_m = \frac{\kappa \times 1000}{M} \quad \text{where M is the molarity of the solution.}$$

The units of Λ_m are :

$$\mathbf{ohm^{-1}\ cm^2\ mol^{-1}} \text{ or } \mathbf{\Omega^{-1}\ cm^2\ mol^{-1}} \text{ or } \mathbf{S\ cm^2\ mol^{-1}}.$$

Example 5.1. *The resistivity of a 0.8 M solution of electrolyte is 5×10^{-3} Ω cm. Calculate its molar conductivity.*

Solution. Here, the resistivity (ρ) $= 5 \times 10^{-3}\ \Omega$ cm

∴ The conductivity of the solution κ $= \frac{1}{\rho} = \frac{1}{5 \times 10^{-3}\ \Omega\ cm} = \frac{1}{5} \times 10^3\ \Omega^{-1}\ cm^{-1}$

Now, molar conductivity is given by $\Lambda_m = \frac{1000 \times \kappa}{M} = 10^3 \times \frac{1}{5} \times 10^3 \times \frac{1}{0.8}$

$$= \mathbf{2.5 \times 10^5\ \Omega^{-1}\ cm^2\ mol^{-1}}.$$

REVIEW PROBLEMS

5.1. Conductivity of two electrolytic solutions A and B each one having a concentration of 0.1 M are 8.5×10^{-2} and 4.1×10^{-4} S cm^{-1} respectively. Which of the two offers less resistance to the flow of current ?

5.2. Calculate conductivity of the 0.02 M solution of an electrolyte having $\Lambda_m = 103$ S cm^2 mol^{-1}.

5.3. Calculate equivalent conductivity of 0.08 N solution of electrolyte having conductivity = 1.72×10^{-3} S cm^{-1}.

5.4. Electrolytic conductivity of 0.02 M solution of KCl at 298 K is 2.48×10^{-2} S cm^{-1}. Calculate its molar conductivity.

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Experimental Measurement of Electrical Conductivity

As pointed out earlier, the conductance of the solution is reciprocal of its resistance. Therefore, if resistance of the solution is known, its conductance can be easily calculated. The resistance of the electrolytic solution is measured with the help of **Wheatstone bridge** method, the arrangement of which has been shown in Fig. 5.1.

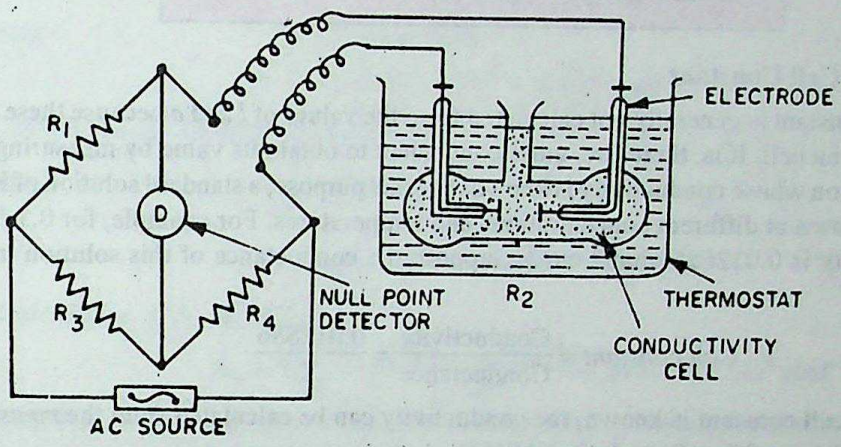

Fig. 5.1. Arrangement of Wheatstone bridge.

The conductivity cell containing solution of electrolyte is made *one arm* of the Wheatstone bridge. The conductivity cell is made of pyrex glass and is fitted with platinum electrodes. These are coated black with finely divided platinum. The fine deposit gives larger surface to the electrodes and improves the sharpness of sound in the null point detector. The cell is placed in thermostat to keep the temperature constant. It is because the conductance changes with the temperature.

After the connections have been made according to Fig. 5.1 ; the alternating current of frequency range 1500—3000 *cps* is employed. *It may be noted that direct current is not used here, because it causes electrolysis and results in the change in concentration of electrolytic solution near the electrodes resulting in polarisation effects.*

The resistances R_1, R_3 and R_4 are so adjusted that a null point is obtained. The null point is indicated by the *detector* D. At this point, $\frac{R_1}{R_2} = \frac{R_3}{R_4}$.

R_2 refers to the resistance of electrolytic solution.

$$R_2 = \frac{R_1 R_4}{R_3}.$$

Knowing the values of R_1, R_3, R_4, the resistance of the electrolytic solution, R_2 is calculated. The reciprocal of R_2 gives the conductance of the solution.

Calculation of Specific Conductance or Conductivity (κ)

It has been pointed out in Section 5.2 that *conductivity* (κ) is related to the *resistance* (R) or conductance (C) as

$$\kappa = \frac{1}{R}\left(\frac{l}{a}\right) = C\left(\frac{l}{a}\right)$$

Here, l is the distance of separation of two electrodes and a is the area of cross-section of the electrodes.

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The quantity l/a is called **cell constant**. The cell constant is expressed in the units cm^{-1}. Knowing the value of *cell constant* and the resistance of the solution, the conductivity can be calculated as

$$\text{Conductivity} = \frac{\text{Cell Constant}}{R}$$

or

$$\boxed{\text{Conductivity} = \text{Conductance} \times \text{Cell constant}}$$

Determination of Cell Constant

The cell constant is generally not calculated from the values of l and a because these are difficult to be measured for a given cell. It is, therefore, more convenient to obtain its value by measuring the conductance of a standard solution whose conductivity is known. For this purpose, a standard solution of KCl is used whose conductivity is known at different concentrations and temperatures. For example, for 0.1 M KCl solution at 298 K, conductivity is 0.012886 ohm^{-1} cm^{-1}. Suppose the conductance of this solution in the given cell is measured to be X.

Then, $$\textit{Cell constant} = \frac{\text{Conductivity}}{\text{Conductance}} = \frac{0.012886}{X}$$

Once, the cell constant is known, the conductivity can be calculated from the *measured conductance or measured resistance* of the electrolytic solution.

Summary of the units of some common properties

Property	*Units*	*Property*	*Units*
Resistance (R)	*ohm* (Ω)	Conductivity or sp. conductance (κ)	$ohm^{-1}\ cm^{-1}$
Resistivity or specific resistance (ρ)	*ohm-cm*	Molar conductivity (Λ_m)	$ohm^{-1}\ cm^2\ mol^{-1}$
Cell constant	cm^{-1}	Equivalent conductivity (Λ_{eq})	$ohm^{-1}\ cm^2\ eq^{-1}$
Conductance (C)	ohm^{-1} (Ω^{-}) or S		

Example 5.2. *The resistance of 0.01N NaCl solution at 25°C is 200 Ω. Cell constant of conductivity cell is unity. Calculate the equivalent conductance.* [A.I. CBSE (O) 1992]

Solution. *Calculation of conductivity*

$$\text{Conductivity } (\kappa) = \frac{1}{R} \times \text{cell constant}$$

$$= \frac{1}{200\ \Omega} \times 1\ cm^{-1} = 5 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$$

Calculation of equivalent conductance

$$\Lambda_{eq} = \frac{\kappa \times 1000}{N} = \frac{5 \times 10^{-3} \times 1000}{0.01} = 5 \times 10^2\ \Omega^{-1}\ cm^2\ eq^{-1}.$$

Example 5.3. *The resistance of a conductivity cell when filled with 0.02 M KCl solution is 164 ohm at 298 K. However, when it is filled with 0.05 M $AgNO_3$ solution its resistance is found to be 78.50 ohms. If conductivity of 0.02 M KCl is 2.768×10^{-3} ohm^{-1} cm^{-1}, calculate*

(i) The conductivity of 0.05 M $AgNO_3$

(ii) The molar conductivity of $AgNO_3$ solution.

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Solution. Step I. *Calculation of cell constant.*

Conductivity of 0.02 M KCl $= 2.768 \times 10^{-3}\ \Omega^{-1}\ cm^{-1}$

Resistance $= 164$ ohm

We know, Conductivity $= \frac{1}{R} \times$ Cell constant

or Cell constant $= R \times$ Conductivity

$= 164 \times 2.768 \times 10^{-3} = \mathbf{0.4539\ cm^{-1}}$.

Step II. *Calculation of conductivity of $AgNO_3$.*

Conductivity $= \frac{1}{R} \times$ Cell constant

$= \frac{1}{78.50} \times 0.4539 = \mathbf{0.00578\ ohm^{-1}\ cm^{-1}}$.

Step III. *Calculation of Λ_m of 0.05 M $AgNO_3$.*

$$\Lambda_m = \frac{1000\ \kappa}{M} = \frac{1000 \times 0.00578}{0.05} = \mathbf{115.6\ \Omega^{-1}\ cm^2\ mol^{-1}}.$$

Example 5.4. *The conductivity of a solution containing 1.0 g of anhydrous $BaCl_2$ (barium chloride) in 200 cm^3 of the solution has been found to be 0.0058 S cm^{-1}. Calculate the molar and equivalent conductivity of the solution. (Atomic masses : Ba = 137 and Cl = 35.5).*

Solution. Conductivity (κ) $= 0.0058\ S\ cm^{-1}$

Molecular mass of $BaCl_2$ $= 137 + 2 \times 35.5 = 208$

Number of moles of $BaCl_2$ in 200 cm^3 of solution $= \frac{1}{208}$ mol

Volume of solution that contains 1 mol of $BaCl_2$ $= 200 \times 208\ cm^3$

Molar conductivity, $\Lambda_m = \kappa V$

where **V** is the volume of solution that contains 1 mol of electrolyte.

$$\Lambda_m = 0.0058 \times 200 \times 208 = \mathbf{241.28\ S\ cm^2\ mol^{-1}}.$$

Equivalent mass of $BaCl_2 = \frac{\text{Molecular mass}}{2} = \frac{208}{2} = 104$

Volume of solution containing one equivalent (*i.e.*, 104 g) of $BaCl_2$

$= 200 \times 104\ cm^3$

Equivalent conductivity, Λ_{eq} $= 0.0058\ S\ cm^{-1} \times 200 \times 104\ cm^3$

$= \mathbf{120.6\ S\ cm^2\ equivalent^{-1}}$.

REVIEW PROBLEMS

5.5. 0.05 M NaOH solution offered a resistance of 31.16 Ω in a conductivity cell at 298 K. If cell constant is 0.367 cm^{-1} find out the molar conductivity of the sodium hydroxide solution.

5.6. 0.5 molar solution of a salt placed between the platinum electrodes 2.0 cm apart and each of area of cross-section 4.0 cm^2 has a resistance of 25 Ω. Calculate the value of Λ_m of solution.

5.7. The conductivity of pure water in a conductivity cell with electrodes of cross-sectional area 4 cm^2 placed at a distance 2 cm apart is 8×10^{-7} S cm^{-1}. Calculate

(*i*) the resistance of conductivity cell

(*ii*) the current that would flow through the cell under the applied potential difference of 1 volt.

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5.8. The resistance of a conductivity cell when filled with 0.1 mole/litre of KCl solution is 8.5 ohms. If the cell constant is 1.1 cm^{-1}, calculate the electrolytic conductivity of 0.1 M solution of KCl.

5.9. The resistance of 0.01 N solution of an electrolyte is 100 ohm at 298 K. Calculate its (*i*) conductance, (*ii*) conductivity and (*iii*) resistivity.

The cell constant is 1 cm^{-1}.

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5.5. VARIATION OF MOLAR CONDUCTIVITY

In general, the conductance of an electrolytic solution depends upon the following factors :

1. *Nature of electrolyte*
2. *Concentration of the solution* and
3. *Temperature.*

1. Nature of electrolyte. The conductance of the solution depends upon the nature of electrolyte. All electrolytes do not ionise in their aqueous solutions to the same extent. They can be divided into two categories depending upon their extent of ionisation.

(*a*) **Strong Electrolytes.** The electrolytes which are completely ionised in aqueous solution are called **strong electrolytes**. Some examples of strong electrolytes are : *mineral acids* like HCl, H_2SO_4, etc., *bases* like NaOH, KOH etc., and *salts* like KCl, NH_4Cl, CH_3COONH_4, etc. Such electrolytes have **high** values of Λ_m.

(*b*) **Weak Electrolytes.** The electrolytes which are not completely ionised in aqueous solution are called **weak electrolytes**. The aqueous solution of weak electrolytes contains ions in equilibrium with undissociated molecules. Some examples of weak electrolytes are CH_3COOH, NH_4OH, etc. Such electrolytes possess **low** values of molar conductivities. The extent to which the weak electrolyte is dissociated in aqueous solution is called its **degree of ionisation** and is denoted by α.

2. Variation of Molar Conductivity with Concentration. In order to understand the variation of molar conductivity with the concentration let us examine the values of Λ_m for some electrolytes at different concentration as given in Table 5.3.

Table 5.3. Molar Conductivity, Λ_m of Electrolytes at 298 K

Concentration	*HCl*	*NaOH*	*NaCl*	*CH_3COOH*	*NH_4OH*
0.1 M	391.32	—	106.74	5.2	3
0.05 M	399.09	—	111.06	7.4	11.3
0.02 M	407.24	—	115.76	11.6	34.0
0.01 M	412.00	238.0	118.51	16.2	46.9
0.005 M	415.80	240.8	120.65	22.8	—
0.001 M	421.366	244.7	123.74	48.6	—
0.0005 M	422.74	245.6	124.50	—	—

From the above table, it is clear that the molar conductivity of electrolytes generally increases with dilution. The relative increase in the molar conductivity in case of strong electrolytes is not so large as that in case of weak electrolytes. The variation of Λ_m versus $\sqrt{c}$ for KCl, a *strong electrolyte* and CH_3COOH, *a weak electrolyte* has been shown in Fig. 5.2.

From Fig. 5.2, it is evident that in case of *strong electrolytes* there is a tendency for molar conductivity to approach a certain limiting value when concentration approaches zero, *i.e.*, when dilution is infinite. *The value of molar conductivity when the concentration approaches zero is known as* **molar conductivity at zero**

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concentration *or* at infinite dilution*. *It is denoted by* Λ_m^∞. In case of *strong electrolytes* the value of Λ_m^∞ is determined by extrapolating the graph to zero concentration (Fig. 5.2).

In the case of *weak electrolytes* such as acetic acid, there is no indication that the limiting value can be attained when the concentration approaches zero. Thus, for weak electrolytes the value of molar conductivity at infinite dilution cannot be obtained by extrapolating the graph to the zero concentration. It may, however, be obtained indirectly by using *Kohlrausch's law.*

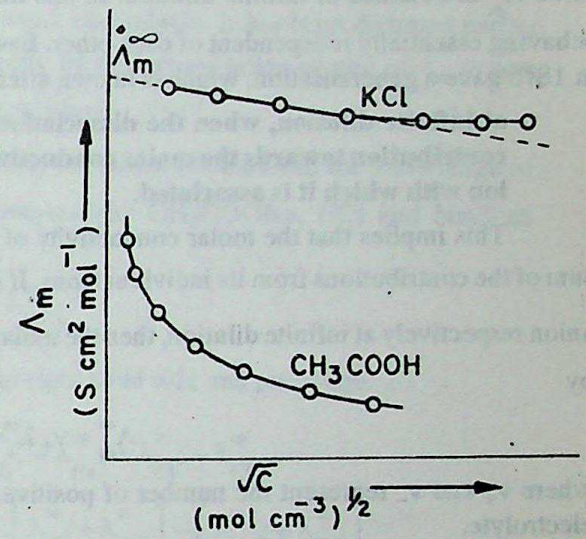

Fig. 5.2. Variation of molar conductivity for KCl and CH_3COOH with concentration.

Explanation for the variation of molar conductivity

(*a*) *For* **weak electrolytes,** the variation in the value of Λ_m with dilution can be explained on the basis of number of ions furnished by it in the solution. The number of ions furnished by the electrolytes in solution depends upon the degree of ionisation of the electrolyte. On dilution, the degree of ionisation of the weak electrolyte increases, thereby increasing the value of Λ_m. Therefore, it is evident that when limiting value of molar conductivity is reached, the degree of dissociation of electrolytes approaches unity *i.e.*, whole of solute dissociates into ions. Therefore, at any other concentration, when the molar conductivity is, Λ_m, the degree of dissociation, α is given by the expression :

$$\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{\text{Molar conductivity at a given concentration}}{\text{Molar conductivity at infinite dilution}}$$

(*b*) *For* **strong electrolytes,** the number of ions in the solution do not increase because, these are almost completely ionised in solution at all concentrations. However, in concentrated solutions of strong electrolytes the density of ions is relatively high which results in the significant *inter-ionic interactions*. Such inter-ionic attractions effectively reduce the speed of the ions and are responsible for lower value of Λ_m. On increasing dilution the ions move apart and inter-ionic attractions are decreased. As a result the value of Λ_m increases. The mathematical relationship between Λ_m and Λ_m^∞ for strong electrolytes was developed by Debye Huckel and Onsager and is known after their name as **Debye Huckel Onsager equation.** The equation in its simplified form can be written as :

$$\Lambda_m = \Lambda_m^\infty - b\sqrt{C}$$

where, Λ_m is molar conductivity,

Λ_m^∞ is molar conductivity at infinite dilution,

b is a constant which depends upon the viscosity and dielectric constant of the solvent,

C is the concentration of solution.

It is quite evident that as C approaches zero $\Lambda_m = \Lambda_m^\infty$.

*The term *infinite dilution* means a solution that is so dilute that it has a maximum or limiting molar conductivity which does not increases on further dilution.

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5.6. KOHLRAUSCH'S LAW

We have already learnt that molar conductivity, Λ_m, of electrolytes increases with dilution till a limiting value Λ_m^∞ is obtained at infinite dilution. In this limit, the positive and negative ions may be thought of as behaving essentially independent of each other. Based upon his exhaustive experimental studies, Kohlrausch in 1875 gave a generalisation, which is known after his name as Kohlrausch's law. It states that :

at infinite dilution, when the dissociation of electrolyte is complete, each ion makes a definite contribution towards the molar conductivity of electrolyte, irrespective of the nature of the other ion with which it is associated.

This implies that the molar conductivity of an electrolyte at infinite dilution can be expressed as the sum of the contributions from its individual ions. If λ_+^∞ and λ_-^∞ represent the molar conductivities of cation and anion respectively at infinite dilution, then the molar conductivity of electrolyte at infinite dilution Λ_m^∞ is given by

$$\Lambda_m^\infty = \nu_+ \lambda_+^\infty + \nu_- \lambda_-^\infty$$

where ν_+ and ν_- represent the number of positive and negative ions furnished by each formula unit of the electrolyte.

For example,

(*i*) One formula unit of NaCl furnishes one Na^+ and one Cl^- ion, therefore,

$$\Lambda_{m(NaCl)}^\infty = \lambda_{Na^+}^\infty + \lambda_{Cl^-}^\infty$$

(*ii*) One formula unit of $BaCl_2$ furnishes one Ba^{2+} and two Cl^- ions, therefore,

$$\Lambda_{m(BaCl_2)}^\infty = \lambda_{Ba^{2+}}^\infty + 2\lambda_{Cl^-}^\infty$$

(*iii*) One formula unit of Na_2SO_4 furnishes two Na^+ ions and one SO_4^{2-} ions, therefore,

$$\Lambda_{m(Na_2SO_4)}^\infty = 2\lambda_{Na^+}^\infty + \lambda_{SO_4^{2-}}^\infty$$

The ionic conductivities at infinite dilution for some ions at 298 K are given in Table 5.4.

Table 5.4. Ionic Conductivities at Infinite Dilution at 298 K

Cation	λ^∞ ($S\ cm^2\ mol^{-1}$)	*Anion*	λ^∞ ($S\ cm^2\ mol^{-1}$)
H^+	349.8	OH^-	198.0
K^+	3.5	Cl^-	76.34
Na^+	50.11	Br^-	78.14
Ag^+	61.9	I^-	76.8
NH_4^+	53.0	NO_3^-	71.4
Cu^{2+}	108.0	CH_3COO^-	40.9
Zn^{2+}	106.0	SO_4^{2-}	159.6

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Applications of Kohlrausch's Law

Some of the important applications of Kohlrausch's law are :

1. Calculation of molar conductivities of weak electrolytes at infinite dilution. Kohlrausch's law is helpful in determining the *limiting molar* conductivities of weak electrolytes. It has been dicussed earlier that value of Λ_m^∞ for weak electrolytes cannot be obtained directly by the extrapolation of plot of Λ_m versus $\sqrt{c}$. But this can be easily calculated with the help of Kohlrausch's law.

For example, the value of Λ_m^∞ for acetic acid (CH_3COOH) can be calculated from the knowledge of the molar conductivities at infinite dilution of strong electrolytes like CH_3COONa, HCl and NaCl as follows :

$$\Lambda^\infty_{m(CH_3COOH)} = \lambda^\infty_{(CH_3COO^-)} + \lambda^\infty_{(H^+)}$$

Now, add and subtract $\lambda^\infty_{Na^+}$ and $\lambda^\infty_{Cl^-}$ to the expression on right hand side and rearrange.

Thus,
$$\Lambda^\infty_{(CH_3COOH)} = \lambda^\infty_{CH_3COO^-} + \lambda^\infty_{H^+} + \lambda^\infty_{Na^+} - \lambda^\infty_{Na^+} + \lambda^\infty_{Cl^-} - \lambda^\infty_{Cl^-}$$
$$= \left[\lambda^\infty_{CH_3COO^-} + \lambda^\infty_{Na^+}\right] + \left[\lambda^\infty_{H^+} + \lambda^\infty_{Cl^-}\right] - \left[\lambda^\infty_{Na^+} + \lambda^\infty_{Cl^-}\right]$$
$$= \Lambda^\infty_{m(CH_3COONa)} + \Lambda^\infty_{m(HCl)} - \Lambda^\infty_{m(NaCl)}$$

In the similar way, $\Lambda^\infty_{m(NH_4OH)} = \Lambda^\infty_{m(NH_4Cl)} + \Lambda^\infty_{m(NaOH)} - \Lambda^\infty_{m(NaCl)}$.

Example 5.5. *The value of Λ_m^∞ of $Al_2(SO_4)_3$ is 858 S cm^2 mol^{-1}, while $\lambda^\infty_{SO_4^{-2}}$ is 160 S cm^2 mol^{-1}. Calculate the value of ionic conductivity of Al^{3+}.*

Solution. According to Kohlrausch's law,

$$\Lambda^\infty_{m(Al_2(SO_4)_3)} = 2\lambda^\infty_{(Al^{3+})} + 3\lambda^\infty_{(SO_4^{2-})}$$
$$858 = 2\lambda^\infty_{(Al^{3+})} + 3 \times 160$$

or
$$2\lambda^\infty_{(Al^{3+})} = 858 - 3 \times 160 = 378 \text{ S cm}^2 \text{ mol}^{-1}$$

or
$$\lambda^\infty_{(Al^{3+})} = \frac{378}{2} = \mathbf{189 \text{ S cm}^2 \text{ mol}^{-1}}.$$

Example 5.6. *The values of Λ_m^∞ for NH_4Cl, NaOH and NaCl at infinite dilution are respectively 129.8, 248.1 and 126.4 ohm^{-1} cm^2 mol^{-1}. Calculate Λ_m^∞ of NH_4OH.*

Solution. According to Kohlrausch's law,

$$\Lambda^\infty_{m(NH_4OH)} = \lambda^\infty_{(NH_4^+)} + \lambda^\infty_{(OH^-)}$$

Add and subtract $\lambda^\infty_{Na^+} + \lambda^\infty_{Cl^-}$ in R.H.S.

$$= \lambda^\infty_{(NH_4^+)} + \lambda^\infty_{(OH^-)} + \lambda^\infty_{(Cl^-)} - \lambda^\infty_{(Cl^-)} + \lambda^\infty_{(Na^+)} - \lambda^\infty_{(Na^+)}$$

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$$= \lambda^{\infty}_{(NH_4^+)} + \lambda^{\infty}_{(Cl^-)} + \lambda^{\infty}_{(Na^+)} + \lambda^{\infty}_{(OH^-)} - \lambda^{\infty}_{(Na^+)} - \lambda^{\infty}_{(Cl^-)}$$

$$= \Lambda^{\infty}_{m(NH_4Cl)} + \Lambda^{\infty}_{m(NaOH)} - \Lambda^{\infty}_{m(NaCl)}$$

$$= 129.8 + 248.1 - 126.4 = 251.5$$

Thus, $\Lambda^{\infty}_{m(NH_4OH)} = \mathbf{251.5\ ohm^{-1}\ cm^2\ mol^{-1}}$.

Example 5.7. *Calculate Λ^{∞}_m for NH_4OH, given that value of Λ^{∞}_m for $Ba(OH)_2$, $BaCl_2$ and NH_4Cl as 523.28, 280.0 and 129.8 S cm^2 mol^{-1} respectively.*

Solution. According to Kohlrausch's law,

$$\Lambda^{\infty}_{m(NH_4OH)} = \lambda^{\infty}_{(NH_4^+)} + \lambda^{\infty}_{(OH^-)}$$

Now, add and subtract $\frac{1}{2}\lambda^{\infty}_{(Ba^{2+})}$ and also $\lambda^{\infty}_{(Cl^-)}$ in R.H.S.

$$\therefore \quad \Lambda^{\infty}_{m(NH_4OH)} = \lambda^{\infty}_{NH_4^+} + \lambda^{\infty}_{(OH^-)} + \frac{1}{2}\lambda^{\infty}_{(Ba^{2+})} - \frac{1}{2}\lambda^{\infty}_{(Ba^{2+})} + \lambda^{\infty}_{(Cl^-)} - \lambda^{\infty}_{(Cl^-)}$$

On rearranging, we get

$$\Lambda^{\infty}_{m(NH_4OH)} = \left[\lambda^{\infty}_{(NH_4^+)} + \lambda^{\infty}_{(Cl^-)}\right] + \left[\frac{1}{2}\lambda^{\infty}_{(Ba^{2+})} + \lambda^{\infty}_{(OH^-)}\right] - \left[\frac{1}{2}\lambda^{\infty}_{(Ba^{2+})} + \lambda^{\infty}_{(Cl^-)}\right]$$

$$= \Lambda^{\infty}_{m(NH_4Cl)} + \frac{1}{2}\Lambda^{\infty}_{m(Ba(OH)_2)} - \frac{1}{2}\Lambda^{\infty}_{m(BaCl_2)}$$

$$= 129.8 + \frac{1}{2} \times 523.28 - \frac{1}{2} \times 280 = \mathbf{251.44\ S\ cm^2\ mol^{-1}}.$$

2. Calculation of degree of dissociation of weak electrolytes. Molar conductivity of weak electrolyte depends upon its degree of dissociation. Higher the degree of dissociation, higher is the molar conductivity. As dilution increases, the degree of dissociation of weak electrolyte also increases and consequently, molar conductivity of electrolyte increases. At infinite dilution molar conductivity becomes maximum because degree of dissociation approaches unity. This is in accrodance with **Ostwald's dilution law** which states *that degree of dissociation of weak electrolyte approaches unity as the concentration of electrolyte in solution approaches zero.*

Thus, if Λ^c_m is the molar conductivity of solution at any concentration and

Λ^{∞}_m is the molar conductivity at infinite dilution.

Then, $$\alpha = \frac{\Lambda^c_m}{\Lambda^{\infty}_m}.$$

Thus, measuring the value of Λ^c_m experimentally, the degree of dissociation of weak electrolyte can be calculated provided value of Λ^{∞}_m is known.

Example 5.8. *The molar conductivities of acetic acid at 298 K at the concentrations of 0.1 M and 0.001 M are 5.20 and 49.2 S cm^2 mol^{-1} respectively. Calculate the degree of dissociation of acetic acid at these concentrations. Given than, $\lambda^{\infty}_{(H^+)}$ (H^+) and $\lambda^{\infty}_{(CH_3COO^-)}$ are 349.8 and 40.9 ohm^{-1} cm^2 mol^{-1} respectively.*

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Solution. Degree of dissociation is given by $\alpha = \frac{\Lambda_m}{\Lambda_m^\infty}$.

Step I. *To calculate* $\Lambda^\infty_{m(CH_3COOH)}$.

$$\Lambda^\infty_{m(CH_3COOH)} = \lambda^\infty_{(CH_3COO^-)} + \lambda^\infty_{(H^+)}$$
$$= 40.9 + 349.8 = 390.7 \text{ ohm}^{-1} \text{ cm}^2 \text{ mol}^{-1}.$$

Step II. *Calculation of degree of dissociation.*

At C = 0.1 M, $\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{5.20}{390.7} = 0.013$ *i.e.,* **1.3%** or α = **1.3%.**

At C = 0.001 M, $\alpha = \frac{\Lambda_m}{\Lambda_m^\infty} = \frac{49.2}{390.7} = 0.125$ *i.e.,* **12.5%.**

Example 5.9. *The resistance of 0.01 M acetic acid solution when measured in a conductivity cell of cell constant 0.366 cm^{-1}, is found to be 2220 Ω. Calculate degree of dissociation of acetic acid at this concentration. Also find the dissociation constant of acetic acid. Given that value of* $\lambda^\infty_{H^+}$ *and* $\lambda^\infty_{CH_3COO^-}$ *as 349.1 and 40.9 Ω^{-1} cm^{-2} mol^{-1} respectively.*

Solution.

Step I. *Calculation of conductivity κ of 0.01 M acetic acid.*

$$\kappa = \frac{1}{R} \times (\text{cell constant}) = \frac{1}{2220\ \Omega} \times 0.366 \text{ cm}^{-1}$$
$$= 1.648 \times 10^{-4}\ \Omega^{-1} \text{ cm}^{-1}.$$

Step II. *Calculation of* Λ_m.

$$\Lambda_m = \frac{\kappa \times 1000}{M} = \frac{1.648 \times 10^{-4} \times 1000}{0.01} = 16.48\ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}.$$

Step III. *Calculation of* Λ_m^∞.

$$\Lambda^\infty_{m(CH_3COOH)} = \lambda^\infty_{H^+} + \lambda^\infty_{CH_3COO^-}$$
$$= 349.1 + 40.9 = 390\ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}.$$

Step IV. *Calculation of degree of dissociation of acetic acid.*

$$\alpha = \Lambda_m / \Lambda_m^\infty = \frac{16.48\ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}}{390\ \Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}} = 0.0422.$$

Step V. *Calculation of dissociation constant (K).*

Dissociation of acetic acid can be represented as

	CH_3COOH	$\rightleftharpoons$ CH_3COO^-	+ H^+
Initial conc.	c mol L^{-1}	—	—
Equilibrium conc.	$c - c\alpha$	$c\alpha$	$c\alpha$

Dissociation constant K is given as $K = \frac{c\alpha \times c\alpha}{c - c\alpha} = \frac{c\alpha^2}{1 - \alpha}$

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Substituting the value of c(0.01 M) and α (0.0422).

$$\therefore \quad K = \frac{0.01 \times (0.0422)^2}{1 - 0.0422} = 1.86 \times 10^{-5}.$$

REVIEW PROBLEMS

5.10. Λ_m^∞ values for NaCl, NaBr and KCl at 298 K are 126.5, 128.2 and 149.9 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively. The ionic conductivity λ^∞ of Br^- ion is 78.1 $ohm^{-1}\ cm^2\ mol^{-1}$. Calculate the value of λ^∞ (K^+).

5.11. Calculate the molar conductivity at infinite dilution of AgCl from the following data :

$$\Lambda_m^\infty (AgNO_3) = 133.4, \Lambda_m^\infty (KCl) = 149.9, \Lambda_m^\infty (KNO_3) = 144.9\ S\ cm^2\ mol^{-1}.$$

5.12. Λ_m for ammonium hydroxide at 0.1, 0.01 and 0.001 M concentrations molar conductivities are 3.6, 11.3 and 34.0 $ohm^{-1}\ cm^2\ mol^{-1}$ respectively. If λ^∞ for NH_4^+ and OH^- ions are 73.1 and 198.0 S $cm^2\ mol^{-1}$ respectively, calculate the degree of dissociation of ammonium hydroxide at different concentrations.

5.13. If Λ_m^∞ of HCl, NaCl and CH_3COONa are 425, 128 and 96 $\Omega^{-1}\ cm^2\ mol^{-1}$ respectively, calculate the value of Λ_m^∞ for acetic acid. *(CBSE 1992)*

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5.7. GALVANIC CELLS

The device in which chemical energy is converted into electrical energy is called **galvanic cell** or **electrochemical cell** or **voltaic cell.** In a galvanic cell, a redox reaction is carried out in an *indirect manner* and the decrease in free energy during the chemical process appears as electrical energy. An indirect redox reaction is such that reduction and oxidation processes are carried out in separate vessels. In order to understand this phenomenon, let us consider the Zn—$CuSO_4$ reaction as the basis of the cell reaction.

In its simple form, a *zinc strip* is dipped in the $ZnSO_4$ solution and a *copper strip* is dipped in the $CuSO_4$ solution taken in separate beakers. The two metallic strips which act as electrodes are connected by the conducting wires through a voltmeter. The two solutions are joined by an inverted U-tube known as **salt bridge.** The U-tube is filled with the solution of some electrolyte such as KCl, KNO_3 or NH_4Cl to which *gelatin* or *agar-agar* has been added to convert it into semi-solid paste. A schematic diagram of this cell has been shwon in Fig. 5.3.

The deflection in voltmeter indicates that there is a potential difference between the two electrodes. It has been found that the conventional current flows through the outer circuit from copper to zinc strip. It implies that the electrons flow occurs from zinc to copper strip.

Let us now understand the working of the cell.

(*i*) Zinc undergoes oxidation to form zinc ions

$$Zn(s) \longrightarrow Zn^{2+}(aq) + 2e^- \ (Oxidation)$$

(*ii*) The electrons liberated during oxidation are pushed through the connecting wires to copper strip.

(*iii*) Copper ions move towards copper strip, pick up the electrons, and get reduced to copper atoms which are deposited at the copper strip.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s) \ (Reduction)$$

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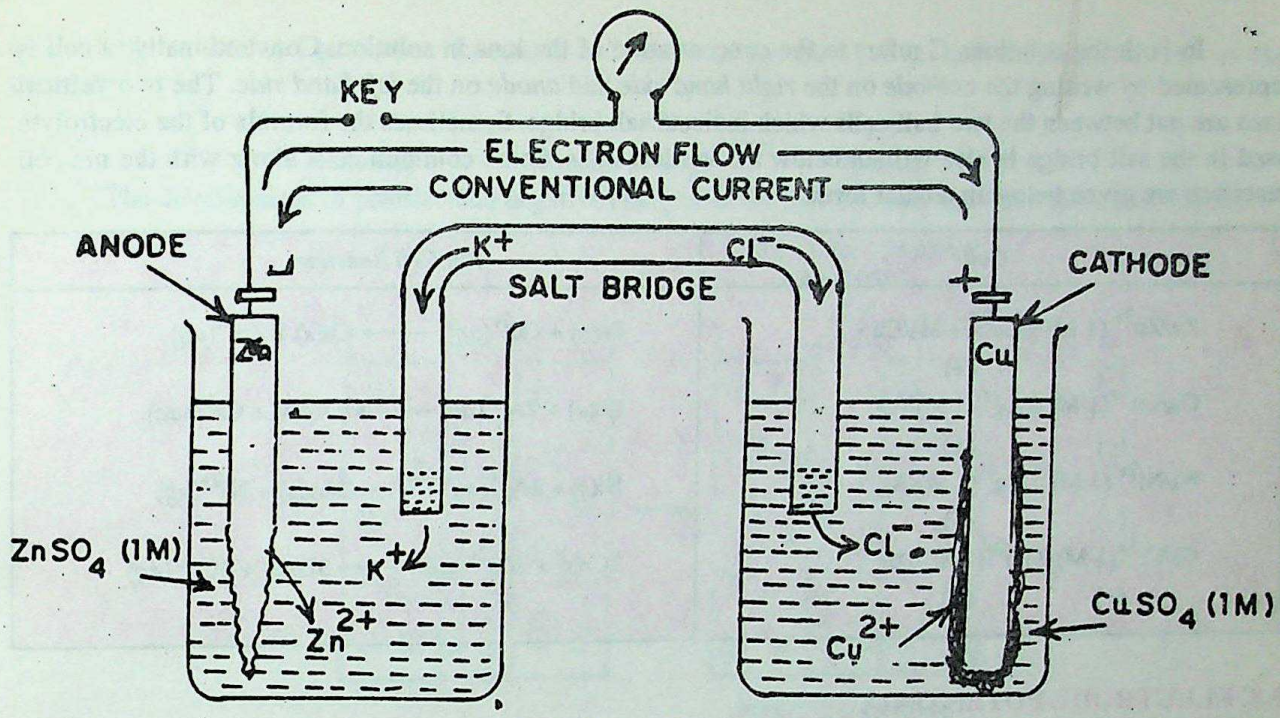

Fig. 5.3. Electrochemical cell.

The electrode at which *oxidation occurs* is **anode** and that at which *reduction occurs* is **cathode.** In the above cell, zinc strip is anode the copper strip is cathode. Due to the oxidation process occurring at the anode it becomes a source of electrons and acquires a negative charge in the cell. Similarly, due to reduction process occurring at the cathode it acquire positive charge and becomes a receiver of the electrons (For details refer to Section 5.8). Thus, in the electrochemical cell,

Anode *constitutes* **– ve terminal** *and*

Cathode *constitutes* **+ ve terminal.**

Function of Salt Bridge. In the electrochemical cell a salt bridge serves two very important functions :

(*i*) *It allows the flow of current by completing the circuit.*

(*ii*) *It maintains electrical neutrality.*

The transference of electrons from *anode* to cathode leads to a net positive charge around the anode due to increase in the concentration of cations and a net negative charge around the cathode due to deposition of positive ions at the cathode. The positive charge around the anode will prevent electrons to flow from it and the negative charge (due to excess of anions in solution) collected around the cathode will prevent acceptance of electrons from the anode. The reaction, thus, stops and no current will flow. The salt bridge comes to aid and restores the electroneutrality of the solutions in the two compartments. It contains a concentrated solution of an *inert electrolyte* the ions of which are not involved in electrochemical reactions. The anions of the electrolyte in the salt bridge migrate to the anode compartment and cations to the cathode compartment. Thus, the salt bridge prevents the accumulation of charges and maintains the flow of current. In the electrochemical cell, the salt bridge can be replaced by the *porous partition* which allows the migration of ions.

Representation of Galvanic Cell

Galvanic cell is a combination of two half cells, namely ; *oxidation half cell* and *reduction half cell.* If M represents the symbol of the element and M^{n+} represents its cation in solution, then

Oxidation half cell is represented as $M/M^{n+}(C)$

Reduction half cell is represented as $M^{n+}(C)/M$.

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In both the notations C refers to the concentration of the ions in solution. Conventionally, a cell is represented by writing the *cathode* on the *right hand side* and *anode* on the *left hand side*. The two vertical lines are put between the two half cells which indicate salt bridge. Sometimes the formula of the electrolyte used in the salt bridge is also written below the vertical lines. Some common cells along with the net cell reactions are given below in tabular form.

Cell	*Net Cell Reaction*
$Zn/Zn^{2+}(1\ M) \parallel Cu^{2+}(1\ M)/Cu$ (–) (+)	$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$
$Cu/Cu^{2+}(1\ M) \parallel Ag^{+}(1\ M)/Ag$ (–) (+)	$Cu(s) + 2Ag^{+}(aq) \longrightarrow 2Ag(s) + Cu^{2+}(aq)$
$Ni/Ni^{2+}(1\ M) \parallel Ag^{+}(1\ M)/Ag$ (–) (+)	$Ni(s) + 2Ag^{+}(aq) \longrightarrow 2Ag(s) + Ni^{2+}(aq)$
$Cr/Cr^{3+}(1\ M) \parallel Pb^{2+}(1\ M)/Pb$ (–) (+)	$2Cr(s) + 3Pb^{2+}(aq) \longrightarrow 3Pb(s) + 2Cr^{3+}(aq)$

5.8. ELECTRODE POTENTIAL

When a strip of metal (M) is brought in contact with the solution containing its own ions (M^{n+}), then either of the following three possible processes can take place :

(*i*) The metal ion M^{n+} may collide with the metallic strip and bounce back without any change.

(*ii*) The metal ion M^{n+} may collide with the strip, gain *n* electrons and get converted into metal atom, *i.e.*, the ion is *reduced.*

$$M^{n+} + ne^- \longrightarrow M$$

(*iii*) The metal atom on the strip may lose *n* electrons and enter the solution as M^{n+} ion, *i.e.*, metal is *oxidised.*

$$M \longrightarrow M^{n+} + ne^-$$

The above changes have been shown in Fig. 5.4.

Now, if the metal has a relatively *high tendency to get oxidised*, its atoms would start losing electrons, change into positive ions and pass into the solution. The electrons lost, accumulate in the metal strip and cause it to develop *negative charge*. The negative charge developed on the strip does not allow metal atoms to continue losing electrons but it would reattract the metal ions from the solution in an attempt to neutralise its charge. Ultimately, a state of equilibrium will be established between the metal and its ions at the interface.

$$\underset{\text{(Metal strip)}}{M} \rightleftharpoons \underset{\text{(Solution)}}{M^{n+}} + \underset{\text{(In metal strip)}}{ne^-}$$

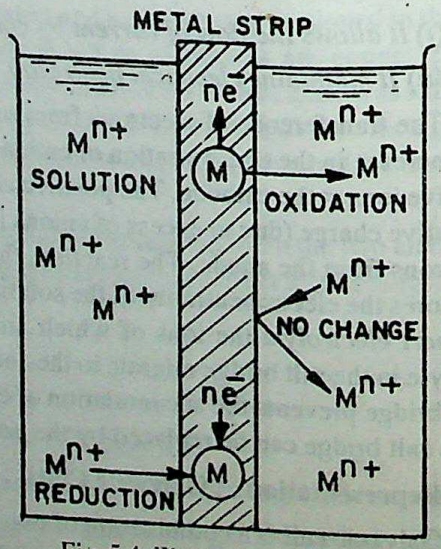

Fig. 5.4. Electrode equilibrium.

Similarly, if the metal ions have relatively *greater tendency to get reduced*, they will accept electrons at the strip from the metal atoms and consequently, a *net positive* charge is developed on the metal strip.

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Ultimately, a similar equilibrium is established between the metal ions and the metal atoms at the interface.

$$\underset{\text{(Solution)}}{M^{n+}} + \underset{\text{(From metal strip)}}{ne^-} \rightleftharpoons \underset{\text{(Metal)}}{M}$$

The development of positive and negative charges on the metallic strip has been shown in Fig. 5.5.

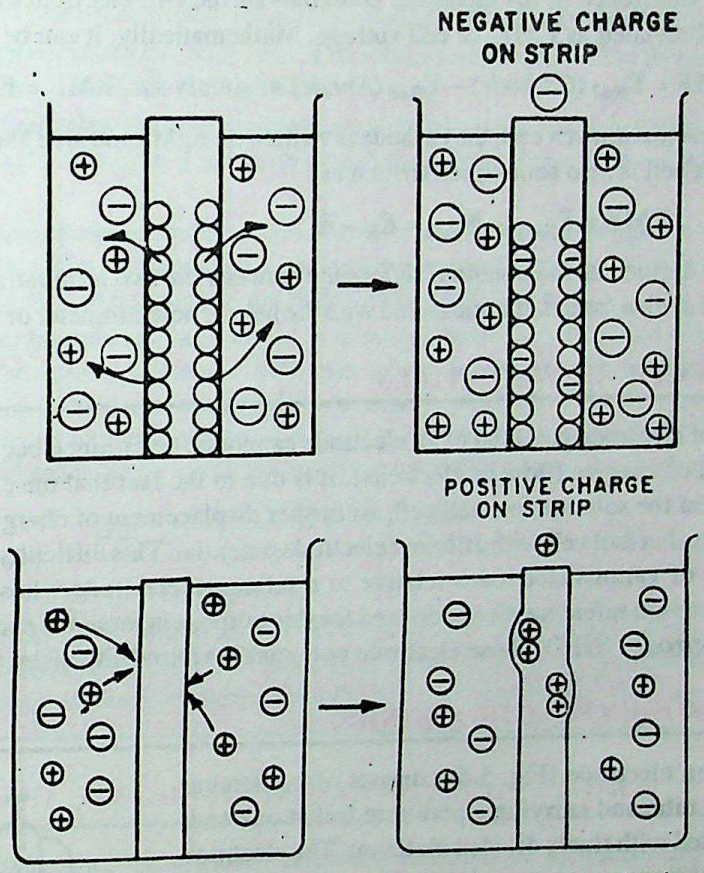

Fig. 5.5. Development of (+)ve or (–)ve charge on the metal strip.

The equilibrium between the metal and its ions leads to the separation of charges*. This results in a potential difference being developed between the metallic strip and its solution.

The electrical potential difference set up between the metal and solution of its ions is known as **half cell electrode potential.** In fact, it is the measure of the tendency of an electrode in a half cell to lose or gain electrons.

According to the present convention, the half reactions are always written as reduction half reactions and their potentials are represented by reduction potentials. It may be noted that :

(*i*) Reduction potential (*tendency to gain electrons*) and oxidation potential (*tendency to lose electrons*) of an electrode are **numerically equal** but have **opposite signs.**

(*ii*) Reduction potential increases with the increase in the concentration of ions and decreases with the decrease in the concentration of the ions in solution.

(*iii*) The reduction potential of electrode when the concentration of the ions in solution is $1\ mol\ L^{-1}$ and temperature is 298 K is called *standard reduction potential* and is represented by $E^\circ_{red.}$

***The net charge separation and hence, the potential difference at equilibrium depends upon :**

the nature of metal and its ion

the concentration of ions in the solution and temperature.

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5.9. EMF OF THE CELL

As discussed earlier, the electrochemical cell consists of two half cells. The electrodes in these half cells have different electrode potentials. When the circuit is completed the loss of electrons occurs at the electrode having lower reduction potential whereas the gain of electrons occurs at the electrode with higher reduction potential. The difference in the electrode potentials of the two electrodes of the cell is termed as **electromotive force** (abbreviated as **EMF**) or **cell voltage.** Mathematically, it can be expressed as

$$\text{EMF} = E_{Red}\,(Cathode) - E_{Red}\,(Anode) \text{ or simply as } \text{EMF} = E_{Cathode} - E_{Anode}$$

Since in the representation of a cell, the cathode is written on right hand side and the anode on left hand side, therefore, EMF of a cell is also sometimes written as :

$$\text{EMF} = E_{Right} - E_{Left} = E_R - E_L$$

EMF of the cell may be defined as the *potential difference between the two terminals of the cell when either no or very little current is drawn from it.* It is measured with the help of potentiometer or vacuum tube voltmeter.

5.10. STANDARD ELECTRODE POTENTIALS

Absolute value of electrode potential of an electrode cannot be determined because a half cell by itself cannot cause movement of charges (flow of electrons). It is due to the fact that once equilibrium is reached between the electrode and the solution in a half cell, no further displacement of charges can occur unless and until it is connected to another half cell with different electrode potential. This difficulty is overcome by finding the electrode potentials of various electrodes relative to a reference electrode whose electrode potential is arbitrarily fixed. The common reference electrode used for this purpose is *standard hydrogen electrode* (**SHE**) or *normal hydrogen electrode* (**NHE**) whose electrode potential is arbitrarility taken to be *zero.*

5.11. NORMAL HYDROGEN ELECTRODE (NHE)

Normal hydrogen electrode (Fig. 5.6) consists of a platinum wire sealed into a glass tube and carrying a platinum foil at one end. The platinum foil is coated with finely divided platinum. The electrode is placed in beaker containing an aqueous solution of some acid having one molar concentration of H^+ ions. Hydrogen gas at one atmospheric pressure is continuously bubbled through the solution at a temperature of 298 K. The oxidation or reduction in the NHE takes place at platinum foil. Hence, it can act as anode as well as cathode and may be represented as :

$$\text{Pt, } \tfrac{1}{2}H_2\ (1\text{ atm})/H^+(1\text{ M}) \quad \text{or} \quad H^+(1\text{ M})/\tfrac{1}{2}H_2\ (1\text{ atm}),\ \text{Pt}$$

respectively.

If NHE acts as anode then oxidation will take place at it as

$$H_2(g) \rightleftharpoons 2H^+(aq) + 2e^-$$

If NHE acts as cathode then reduction will take place at it as

$$2H^+(aq) + 2e^- \rightleftharpoons H_2(g)$$

The electrode potentials of other electrodes are determined by coupling them with NHE. *The electrode potential of an electrode determined relative to the standard hydrogen electrode under standard*

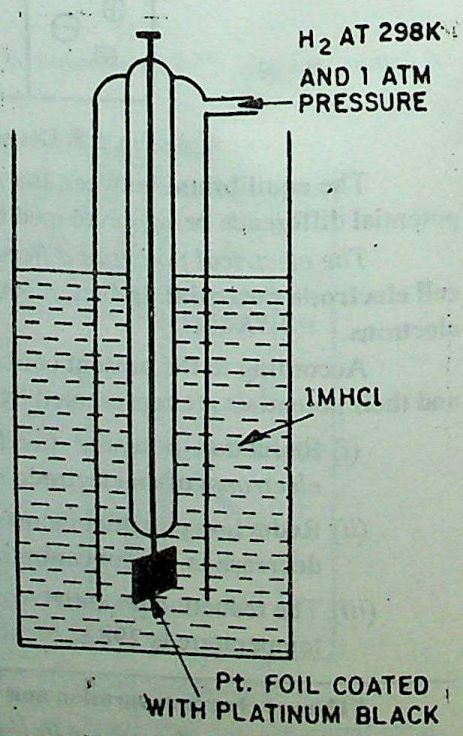

Fig. 5.6. Normal hydrogen electrode (NHE).

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conditions is called **standard electrode potential.** It is represented as E°. The standard conditions are 1 M concentration of ions at 298 K temperature and 1 atmospheric pressure.

DIFFERENT TYPES OF ELECTRODES

Some important types of electrodes which are frequently used in electrochemical cells are described as follows.

1. Metal-metal ion electrode. Such type of electrodes include a metal rod dipped in the solution of its own ions. Some examples are **Zn/Zn^{2+}, Ag/Ag^{+}, Cu/Cu^{2+}** etc.

2. Amalgam electrodes. These are similar to metal-metal ion electrodes, but here the metal is used in the form of its amalgam with Hg. Amalgam is formed to modify the activity of metal. **$Zn—Hg/Zn^{2+}$** is one of the common example of this type.

3. Gas electrodes. Such electrodes involve inert metal such as platinum dipped in the solution containing ions of the gaseous element. The arrangement is made in such a manner that gas and its ions are brought is contact at the surface of the inert metal. Some examples are **H_2/H^{+}, Pt or Cl_2/Cl^{-1}, Pt.**

4. Metal-metal insoluble salt-salt anion. In this of electrodes, the metal and some sparingly soluble salt of metal is dipped in the aqueous solution of some other soluble salt whose anion is same as that of sparingly soluble salt of the metal. One of the common example is **Ag-AgCl(s)/KCl(aq)**. Here, silver and sparingly soluble salt of Ag, *i.e.*, AgCl is put in aqueous solution of KCl. The conc. of Ag^{+} ions in KCl solution is controlled by the concentration of KCl and it can be calculated from the knowledge of K_{sp} of AgCl as follows.

$$[Ag^{+}] = \frac{K_{sp} \text{ of AgCl}}{[Cl^{-}]} = \frac{K_{sp} \text{ of AgCl}}{[KCl]}$$

Other examples of this type of electrodes are

$Hg—Hg_2Cl_2/KCl\ (aq)$ (Calomel electrode) and ***$Pb—PbSO_4/K_2SO_4(aq)$***, etc.

4. Redox electrodes. These electrodes include a platinum wire dipped in a solution of a mixture of two salts of the same metal having different oxidation states *Pt, Fe^{2+}/Fe^{3+} and Pt, Sn^{2+}/Sn^{4+}* are some examples.

5.12. MEASUREMENT OF STANDARD ELECTRODE POTENTIALS

In order to determine the standard electrode potential of an electrode, the electrode in standard conditions is connected to normal hydrogen electrode to constitute a cell. *If the electrode forms the negative terminal of the cell it is allotted negative electrode potential and if it forms the positive terminal of the cell, it is allotted a positive value of electrode potential.* The potential difference between the electrodes is determined with the help of *potentiometer or vacuum tube voltmeter* as mentioned earlier. At the same time, the direction of flow of conventional current in the external circuit is also noticed with the help of galvanometer: This helps us to know the positive and negative terminals of the cell because conventional current in the external circuit flows from +ve terminal to –ve terminal. Now, the direction of the flow of electrons is opposite to that of conventional current. Since electron flow in external circuit occurs from *anode* to *cathode* it helps us to mark anode and cathode electrodes of the cell.

$$E°_{Cell} = E°_{Cathode} - E°_{Anode}$$

Knowing the $E°_{cell}$ and electrode potential of one of the electrodes (NHE), that of the other can be calculated.

For example, in order to find out standard electrode potential of zinc electrode, zinc electrode containing 1 M concentration of Zn^{2+} ions is connected to NHE. The voltmeter reading shows the potential difference ($E°_{cell}$) of 0.76 volts. The electron flow is found to be from zinc electrode to NHE. From this it follows that Zn acts as anode while NHE acts as cathode. The net cell reaction is

$$Zn(s) + 2H^{+}(aq) \longrightarrow Zn^{2+}(aq) + H_2(g)$$

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Now,
$$E^\circ_{Cell} = E^\circ_{Cathode} - E^\circ_{Anode}$$
$$= E^\circ_{H^+/\frac{1}{2}H_2} - E^\circ_{Zn^{2+}/Zn},\ 0.76 = 0 - E^\circ_{Zn^{2+}/Zn}$$
$$E^\circ_{Zn^{2+}/Zn} = -\mathbf{0.76\ volts.}$$

Similarly, when standard copper electrode is coupled with **NHE** the voltmeter reading shows a potential difference (E°_{cell}) of 0.34 volts. The electron flow is found to occur from NHE towards copper electrode. Therefore, NHE in this cell acts as *anode* and copper electrode acts as cathode. The cell reaction is

$$Cu^{2+}(aq) + H_2(g) \longrightarrow Cu(s) + 2H^+(aq)$$
$$E^\circ_{Cell} = E^\circ_{Cathode} - E^\circ_{Anode}$$
$$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{H^+/\frac{1}{2}H_2}$$
$$0.34 = E^\circ_{Cu^{2+}/Cu} - 0$$
$$E^\circ_{Cu^{2+}/Cu} = \mathbf{0.34\ volts.}$$

The standard reduction potentials of other electrodes including metals as well as non-metals can be determined in the similar way. For example, the standard electrode potential of chlorine can be determined by using electrode consisting of Cl_2 gas at one atmospheric pressure and 298 K in equilibrium with 1 M solution of Cl^- ions. For metals of variable valency, the redox potential of one ion in equilibrium with the other ion of different charge can also be determined. For example, redox potential of $Fe^{3+}(aq)/Fe^{2+}(aq)$ can be determined by using the cell

$$Pt, \tfrac{1}{2}H_2(g)/H^+\ (1\ M) \,||\, Fe^{3+}(M), Fe^{2+}(1\ M)/Pt$$

It is not always convenient to use NHE as a reference electrode because of the following difficulties :

(*i*) Unity concentration of H^+ ions is difficult to be maintained,

(*ii*) 1 atm. pressure of H_2 gas cannot be maintained uniformly,

(*iii*) The hydrogen electrode gets poisoned even if traces of impurities are present.

To overcome these difficulties some other electrodes like calomel electrodes of silver-silver chloride are used as reference electrodes. The standard electrode potentials of these electrodes are given below.

Calomel electrode : $Hg - Hg_2Cl_2/KCl\ (aq)$; $E^\circ_{Red} = 0.2422$ V

Silver-silver salt electrode : $Ag - AgCl(s)/KCl(aq)$; $E^\circ_{Red} = 0.2225$ V

5.13. ELECTROCHEMICAL SERIES

We have seen that different *metal/metal ion* combinations have different values of electrode potentials. The various elements can be arranged in order of increasing or decreasing values of their reduction potentials. *The arrangement of various elements in the order of increasing values of standard reduction potentials* is called **electrochemical series.** The electrochemical series, also called activity series consisting of some electrodes along with their respective reduction reactions has been given in Table 5.5.

5.14. NERNST EQUATION FOR ELECTRODE POTENTIAL AND CELL POTENTIAL

It has been pointed out earlier that the tendency of metal to lose electron or tendency of its ions to gain electrons depends upon the concentration of the ions in solution. At the same time, the tendency to lose or gain electrons is expressed in terms of electrode potentials. The value of electrode potential, therefore, changes with the variation in the concentration of the ions. The quantitative relationship between the concentration of ions and electrode potentials is given by **Nernst equation.** For a general electrode reaction :

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Table 5.5. Standard Electrode Potentials

Elements	Electrode reaction	E°_{red} (volts)
Li	$Li^+(aq) + e^- \longrightarrow Li(s)$	– 3.05
K	$K^+(aq) + e^- \longrightarrow K(s)$	– 2.93
Ba	$Ba^{2+}(aq) + 2e^- \longrightarrow Ba(s)$	– 2.90
Ca	$Ca^{2+}(aq) + 2e^- \longrightarrow Ca(s)$	– 2.87
Na	$Na^+(aq) + e^- \longrightarrow Na(s)$	– 2.71
Mg	$Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$	– 2.37
Al	$Al^{3+}(aq) + 3e^- \longrightarrow Al(s)$	– 1.66
Zn	$Zn^{2+}(aq) + 2e^- \longrightarrow Zn(s)$	– 0.76
Cr	$Cr^{3+}(aq) + 3e^- \longrightarrow Cr(s)$	– 0.74
Fe	$Fe^{2+}(aq) + 2e^- \longrightarrow Fe(s)$	– 0.44
	$H_2O(l) + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$	– 0.41
Cd	$Cd^{2+}(aq) + 2e^- \longrightarrow Cd(s)$	– 0.40
Pb	$PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$	– 0.31
Co	$Co^{2+}(aq) + 2e^- \longrightarrow Co(s)$	– 0.28
Ni	$Ni^{2+}(aq) + 2e^- \longrightarrow Ni(s)$	– 0.25
Sn	$Sn^{2+}(aq) + 2e^- \longrightarrow Sn(s)$	– 0.14
Pb	$Pb^{2+}(aq) + 2e^- \longrightarrow Pb(s)$	– 0.13
H_2	**$2H^+ + 2e^- \longrightarrow H_2(g)$ (standard electrode) 0.00**	
Cu	$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$	+ 0.34
I_2	$I_2(s) + 2e^- \longrightarrow 2I^-(aq)$	+ 0.54
Fe	$Fe^{3+} + e^- \longrightarrow Fe^{2+}(aq)$	+ 0.77
Hg	$Hg_2^{2+}(aq) + 2e^- \longrightarrow 2Hg(l)$	+ 0.79
Ag	$Ag^+(aq) + e^- \longrightarrow Ag(s)$	+ 0.80
Hg	$Hg^{2+}(aq) + 2e^- \longrightarrow Hg(l)$	+ 0.85
N_2	$NO_3^- + 4H^+ + 3e^- \longrightarrow NO(g) + 2H_2O$	+ 0.97
Br_2	$Br_2(aq) + 2e^- \longrightarrow 2Br^-(aq)$	+ 1.08
O_2	$O_2(g) + 2H_3O^+(aq) + 2e^- \longrightarrow 3H_2O$	+ 1.23
Cr	$Cr_2O_7^{2-} + 14H^+ + e^- \longrightarrow 2Cr^{3+} + 7H_2O$	+ 1.33
Cl_2	$Cl_2(g) + 2e^- \longrightarrow 2Cl^-(aq)$	+ 1.36
Au	$Au^{3+}(aq) + 3e^- \longrightarrow Au(s)$	+ 1.42
Mn	$MnO_4^-(aq) + 8H_3O^+(aq) + 5e^- \longrightarrow Mn^{2+}(aq) + 12H_2O(l)$	+ 1.51
F_2	$F_2(g) + 2e^- \longrightarrow 2F^-(aq)$	+ 2.87

Increasing (a) tendency for oxidation to occur (b) Power as reducing agent ↑

Increasing (a) tendency for reduction to occur (b) Power as oxidising agent ↓

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$$M^{n+} + ne^- \longrightarrow M$$

the Nernst equation can be written as

$$E_{(M^{n+}/M)} = E^\circ_{(M^{n+}/M)} + \frac{RT}{nF} \ln \frac{[M^{n+}]}{[M]}$$

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} + \frac{2.303\ RT}{nF} \log \frac{[M^{n+}]}{[M]} \quad ...(5.1)$$

where $E_{M^{n+}/M}$ = Electrode potential

$E^\circ_{M^{n+}/M}$ = Standard electrode potential with reference to SHE when conc. of M^{n+} is 1 mol L^{-1}

$R = 8.314\ JK^{-1}\ mol^{-1}$

T = Temperature

$[M^{n+}]$ = Molar concentration of ions*

n = No. of electrons gained

F = 96500 coulombs

[M] = Concentration of metal*

Substituting these values in equation (5.1), we get

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} + \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[M^{n+}]}{[M]}$$

$$= E^\circ_{M^{n+}/M} + \frac{0.059}{n} \log \frac{[M^{n+}]}{[M]} \quad ...(5.2)$$

In general, for any electrode,

$$E_{red} = E^\circ_{red} + \frac{0.059}{n} \log \frac{\text{[Oxidised state]}}{\text{[Reduced state]}}$$

It may be noted that concentration of solid phase is taken to be unity.

Example 5.10. *What is the electrode potential of Mg^{2+}/Mg electrode in which conc. of Mg^{2+} is 0.01 M ? $E^\circ_{Mg^{2+}/Mg} = -2.36$ V.*

Solution. $Mg^{2+}(aq) + 2e^- \longrightarrow Mg(s)$

$$E_{Mg^{2+}/Mg} = E^\circ_{Mg^{2+}/Mg} + \frac{0.059}{2} \log \frac{[Mg^{2+}]}{[Mg]}$$

$$[Mg^{2+}] = 0.01\ M\ ;\ [Mg] = 1$$

$$E_{Mg^{2+}/Mg} = -2.36 + \frac{0.059}{2} \log (0.01) = \mathbf{-2.42\ V.}$$

Example 5.11. *Calculate the E_{red} of the following electrode :*

$$Pt,\ Cl_2\ (1.5\ atm)/2\ Cl^-\ (0.01\ M)\ ;\ E^\circ_{Cl_2/2Cl^-} = 1.36\ V.$$

Solution. The electrode reaction is

$$Cl_2(g) + 2e^- \longrightarrow 2Cl^-$$

*Truly speaking activities of various species should be used in Nernst equation. The activity of a gas is assumed to be equal to its respective *partial pressures* and that of aqueous ion is taken to be its *molar concentration per litre*. The detailed discussion of activity is beyond the scope of the book.

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$$E = E^\circ + \frac{0.059}{2}\log\frac{[Cl_2]}{[Cl^-]^2} = E^\circ + \frac{0.059}{2}\log\frac{p_{Cl_2}}{[Cl^-]^2}$$

$$= 1.36 + 0.0295\log\frac{1.5}{(0.01)^2} = 1.36 + 0.0295 \times 4.1761$$

$$= 1.36 + 0.1231 = \mathbf{1.483\ V.}$$

REVIEW PROBLEMS

5.14. Calculate the half cell potential for Zn^{2+} (0.095 M)/Zn, given that $E^\circ_{Zn^{2+}/Zn} = -0.76$ V.

5.15. At what of pH of HCl solution will hydrogen gas electrode show electrode potential of – 0.118 V ? H_2 gas is bubbled at 298 K and 1 atm pressure.

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Calculation of cell potential

Let us apply equation (5.2) for the calculation of cell potential of some galvanic cells.

1. **Zn/Zn^{2+} (*aq*) || Cu^{2+}(*aq*)/Cu**

Cell potential $= E_{cathode} - E_{anode}$

$$= E_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn} \quad ...(i)$$

Using Nernst equation for **copper electrode**

$$E_{Cu^{2+}/Cu} = E^\circ_{Cu^{2+}/Cu} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Cu]}$$

Similarly, for **zinc electrode**

$$E_{Zn^{2+}/Zn} = E^\circ_{Zn^{2+}/Zn} + \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Zn]}$$

Substituting these values in (*i*),

Cell Potential $= E^\circ_{Cu^{2+}/Cu} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Cu]} - E^\circ_{Zn^{2+}/Zn} - \frac{0.059}{2}\log\frac{[Zn^{2+}]}{[Zn]}$

$$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Zn^{2+}/Zn} + \frac{0.059}{2}\log\frac{[Cu^{2+}][Zn]}{[Cu][Zn^{2+}]}$$

Since concentration of solids is taken to be unity

$\therefore$ $[Zn] = [Cu] = 1$

Cell potential $= E^\circ_{Cell} + \frac{0.059}{2}\log\frac{[Cu^{2+}]}{[Zn^{2+}]}$

In general, for a redox cell reaction involving the transference of *n* electrons

$$aA + bB \longrightarrow cC + dD$$

$$E_{cell} = E^\circ_{cell} + \frac{RT}{nF}\ln\frac{[A]^a[B]^b}{[C]^c[D]^d} \quad ...(5.3)$$

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Equation (5.3) can be simplified by substituting the values of R (8.314 JK^{-1} mol^{-1}, T (298 K) and F (96500 coulombs) as follows :

$$E_{cell} = E^\circ_{cell} + \frac{2.303 \times 8.314 \times 298}{n \times 96500} \log \frac{[A]^a [B]^b}{[C]^c [D]^d}$$

$$\mathbf{E_{cell} = E^\circ_{cell} + \frac{0.059}{n} \log \frac{[A]^a [B]^b}{[C]^c [D]^d}} \quad ...(5.4)$$

While using equation (5.3), the following points must be kept in mind :

(*i*) *Concentration of solids (metals) is taken to be unity.*

(*ii*) *Concentrations of ionic species are taken in* **mol L^{-1}.**

(*iii*) *Concentrations of gases are expressed in terms of their respective* **partial pressures** *in atmospheres.*

The values of *n, a, b, c, d* are obtained from the **balanced cell reaction.** For example, let us consider the cell,

$$Zn/Zn^{2+} \parallel Ag^+/Ag$$

The balanced cell reaction is

$$2Ag^+(aq) + Zn(s) \longrightarrow 2Ag(s) + Zn^{2+}(aq)$$

Here, $n = 2$

$$\therefore \quad E_{cell} = E^\circ_{cell} + \frac{0.059}{2} \log \frac{[Ag^+]^2 [Zn]}{[Zn^{2+}][Ag]^2}$$

$$[Ag] = [Zn] = 1$$

Similarly, for the cell,

$Al/Al^{3+} \parallel Ni^{2+}/Ni$, the cell reaction is

$$2Al(s) + 3Ni^{2+}(aq) \longrightarrow 3Ni(s) + 2Al^{3+}(aq)$$

Here, $n = 6$

$$\therefore \quad E_{cell} = E^\circ_{cell} + \frac{0.059}{2} \log \frac{[Ni^{2+}]^3 [Al]^2}{[Al^{3+}]^2 [Ni]^3}$$

$$[Ni] = [Al] = 1$$

Let us now apply equation (5.4) to some numerical problems.

Example 5.12. *Calculate the e.m.f. of the cell with cell reaction :*

$$Cu + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$$

when $[Cu^{2+}] = 0.130$ *M and* $[Ag^+] = 1 \times 10^{-2}$ *M. The values of* $E^\circ_{Cu^{2+}/Cu}$ *and* $E^\circ_{Ag/Ag}$ *are given to be 0.34 V and 0.80 V respectively.*

Solution. The cell is represented as

$$\underset{(-)\,Anode}{Cu/Cu^{+2}_{(0.13\,M)}} \parallel \underset{(+)\,Cathode}{Ag^+_{(10^{-2}\,M)}/Ag}$$

From the cell reaction it is clear that the value of $n = 2$.

By applying equation (5.4), we get

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{2} \log \frac{[Cu][Ag^+]^2}{[Cu^{2+}][Ag]^2} \quad ...(i)$$

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Now $[Ag] = [Cu] = 1$ being solids.

Also $E^\circ_{cell} = E^\circ_{Ag^+/Ag} - E^\circ_{Cu^{2+}/Cu} = 0.80 - 0.34 = 0.46$ V

Substituting the value of E°_{cell} in (*i*),

$$E_{cell} = 0.46 + \frac{0.059}{2}\log\frac{[Ag^+]^2}{[Cu^{2+}]} = 0.46 + \frac{0.059}{2}\log\frac{[1\times10^{-2}]^2}{0.130}$$

$$= 0.46 + \frac{0.059}{2}\log\frac{1\times10^{-4}}{0.130} = 0.46 + \frac{0.059}{2}\log(7.692\times10^{-4})$$

$$= 0.46 + \frac{0.059}{2}[-4 + 0.8861] = 0.46 - 0.092 = \mathbf{0.368\ V.}$$

REVIEW PROBLEMS

5.16. The reduction potentials of Cu^{2+}/Cu and Ag^+/Ag electrodes are 0.34 V and 0.80 V respectively. Construct a galvanic cell using these E°_{Red} values. For what concentration of Ag^+ ions will e.m.f. of the cell at 25°C be zero if conc. of Cu^{2+} is 0.01 M. *(I.I.T. J.E.E. 1990)*

5.17. Calculate the cell potential of the following cell :

$$Cr/Cr^{3+}_{(0.01\ M)} \parallel Fe^{3+}_{(0.01\ M)}/Fe$$

$E^\circ_{Cr^{3+}/Cr} = -0.74$ V ; $E^\circ_{Fe^{2+}/Fe} = -0.44$ V. *(C.B.S.E. 1993)*

5.18. A cell is constituted by dipping a zinc plate in 0.1 M zinc nitrate solution and a lead plate in 0.02 M lead nitrate solution. Calculate the EMF of the cell, if

$E^\circ_{Pb^{2+}/Pb} = -0.13$ V and $E^\circ_{Zn^{2+}/Zn} = -0.76$ V.

5.19. Calculate cell potential for the following cell :

$$Pb/Pb^{2+}(1\times10^{-3}\ M) \parallel Pt, \tfrac{1}{2}Cl_2\ (1\ atm)/Cl^-\ (0.1\ M)$$

Given that $E^\circ_{Pb^{2+}/Pb} = -0.13$ V and $E^\circ_{\frac{1}{2}Cl_2/Cl^-} = 1.358$ V.

5.20. A cell is constituted by cadmium and nickel electrodes as

$$Cd/Cd^{2+}\ (?) \parallel Ni^{2+}\ (2.0\ M)/Ni$$

The EMF of the cell is found to be 0.20 V. Calculate the concentration of Cd^{2+} ions in the solution. Use the values of standard reduction potentials from Table 5.5.

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Concentration Cells

These are the galvanic cells in which the electrodes are made of same metal but they have different concentration of electrolytes. The difference in the concentration of electrolytes creates potential difference across the two electrodes. *The electrode with smaller concentration of electrolyte acts as anode or – ve terminal, whereas the electrode with larger concentration of electrolyte acts as cathode or + ve terminal.* Some examples are

(*i*) $Cu(s)/Cu^{2+}$ (0.01 M) $\parallel Cu^{2+}$(0.1 M)/Cu

(*ii*) Pt, H_2/H^+ (0.01 M) $\parallel H^+$ (0.2 M)/H_2, Pt

In general, if C_2 is the concentration of electrolyte in cathodic half an C_1 is the concentration of electrolyte in anodic half cell, then the net cell voltage at 298 K is given by

$$E_{cell} = \frac{0.059}{n}\log\frac{C_2}{C_1}$$

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5.15. NERNST EQUATION AND EQUILIBRIUM CONSTANT

It is a well known fact that the galvanic cell does not continue working indefinitely and *stops working after some time*. In fact, as the cell reaction progresses, there is a fall in the concentration of cations around cathode due to reduction and at the same time there is an increase in the concentration of metal cations around anode due to oxidation. Consequently, electrode potential of cathode decreases and that of anode increases with the passage of time. Ultimately, a stage reaches when the potential difference ($E_{cathode} - E_{anode}$) becomes zero and there is no flow of electrons. For example :

In a cell, $Zn/Zn^{2+}(aq) \parallel Cu^{2+}(aq)/Cu$, the flow of electrons from zinc to copper stops when $E_{Zn^{2+}/Zn}$ becomes equal to $E_{Cu^{2+}/Cu}$.

In this situation the concentration of $Zn^{2+}(aq)$ and that of $Cu^{2+}(aq)$ will be equilibrium concentrations because the cell reaction attains equilibrium

$$Zn(s) + Cu^{2+}(aq) \rightleftharpoons Zn^{2+}(aq) + Cu(s)$$

Considering the concentrations of Zn(*s*) and Cu(*s*) to be unity, the equilibrium constant for the above reaction, K_c, is given by the expression

$$K_c = \frac{[Zn^{2+}]}{[Cu^{2+}]} \qquad [\because \ [Cu] = [Zn] = 1]$$

Applying the Nernst equation for cell potential (Eq. 5.4)

$$E_{cell} = E^\circ_{cell} + \frac{2.303\ RT}{nF} \log \frac{[Cu^{2+}]}{[Zn^{2+}]}$$

or

$$E_{cell} = E^\circ_{cell} - \frac{2.303\ RT}{nF} \log \frac{[Zn^{2+}]}{[Cu^{2+}]}$$

Since E_{cell} at equilibrium is zero

$$\therefore \quad 0 = E^\circ_{cell} - \frac{2.303\ RT}{nF} \log K_c$$

or

$$E^\circ_{cell} = \frac{2.303\ RT}{nF} \log K_c$$

$$\log K_c = E^\circ_{cell} \times \frac{nF}{2.303\ RT} = E^\circ_{cell} \times \frac{n \times 96500}{2.303 \times 8.314 \times 298} = E^\circ_{cell} \times \frac{n}{0.059}$$

$$\therefore \quad \boxed{\log K_c = \frac{n}{0.059} \times E^\circ_{cell}} \qquad ...(5.6)$$

or

$$\boxed{E^\circ_{cell} = \frac{0.059}{n} \log K_c} \qquad ...(5.7)$$

Significance of K_c. The value of K_c gives the extent of the cell reaction. For example, the value of K_c for the Zn-$CuSO_4$ cell reaction at 298 K is 2×10^{37}, which shows that the reaction has proceeded almost to completion.

Example 5.13. *Calculate the equilibrium constant for a reaction, $Ni(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Ni^{2+}(aq)$. Given the values of $E^\circ_{Ni^{2+}/Ni}$ and $E^\circ_{Cu^{2+}/Cu}$ as – 0.25 and + 0.34 V respectively.*

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Solution. Step I. *Calculation of* E°_{cell}

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$

$$= E^\circ_{Cu^{2+}/Cu} - E^\circ_{Ni^{2+}/Ni} = 0.34 - (-0.25) = 0.59 \text{ V}.$$

Step. II. *Calculation of* K_c

$$\log K_c = \frac{n}{0.059} \times E^\circ_{cell}$$

Here, $n = 2$

$$\log K_c = \frac{2}{0.059} \times 0.59 = 20$$

$$K_c = 1 \times 10^{20}.$$

REVIEW PROBLEMS

5.21. Calculate at 25°C the equilibrium constant for the reaction $Cu(s) + 2Ag^+(aq) \longrightarrow Cu^{2+}(aq) + 2Ag(s)$ [At 25°C, $E^\circ_{cell} = 0.47$ V, R = 8.314 JK^{-1} mol^{-1}, F = 96500 C]. **[*CBSE 1992*]**

5.22. Calculate the equilibrium constant, K for the reaction

$$3Sn^{4+} + 2Cr \longrightarrow 3Sn^{2+} + 2Cr^{3+}; \; E^\circ = 0.885 \text{ V}.$$

5.23. Calculate equilibrium constant for the reaction

$$Cl_2(g) + 2I^-(aq) \longrightarrow 2Cl^-(aq) + I_2(s)$$

Given that $E^\circ_{Cl_2/2Cl^-} = 1.36$ V and $E^\circ_{I_2/2I} = 0.536$ V.

5.24. A cell is constructed on the basis of following half reactions

$$Au(s) + 4Cl^- \longrightarrow AuCl_4^- + 3e^-; \; E^\circ_{oxi} = -1.00 \text{ V}$$

$$Au^{3+} + 3e^- \longrightarrow Au(s); \; E^\circ_{Red} = +150 \text{ V}$$

E°_{cell} is determined to be 0.50 volts. Calculate the equilibrium constant for the reaction

$$Au^{3+} + 4Cl^- \rightleftharpoons AuCl_4^-.$$

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5.16. ELECTROCHEMICAL CELL AND FREE ENERGY

A galvanic cell is a source of electrical energy which can be used for different kinds of work. Unlike heat energy, the electrical energy can be quantitatively converted into work. The *electrical work* or the *electrical energy* is equal to the product of EMF of the cell and the electrical charge that flows through the external wire.

It may be put as W_{Elec} = (EMF) (Electrical charge flowing through the wire).

If n is the number of moles of electrons flowing through the wire and F is 1 faraday of electricity, then

Charge flowing through the wire = nF

If E_{cell} is the EMF of the cell, then $W_{Elec} = nF \times E_{cell}$ ...(5.8)

We have learnt in **Unit 4** that the free energy change (ΔG) for a process occurring at constant temperature T and pressure P is the measure of useful work that can be obtained. Mathematically,

$$\Delta G = W_{non\text{-}expansion}$$

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For electrical systems, $W_{non\text{-}expansion}$ can be written as W_{Elect}, because work involved is electrical work. In electrochemical cells the work is done by the system and by conventions it is taken to be negative. Thus, electrical work performed by the cell can be written as $-W_{elec}$.

Now, equating free energy change (ΔG) to the electrical work done by the cell ($-W_{Elec}$), we have

$$\Delta G = -W_{Elec} = -nFE_{cell} \quad ...(5.9) \quad (\because \; W_{Elec} = nFE_{cell})$$

For the sake of comparison, standard cell potentials are used. Therefore, standard free energy change is given by

$$\boxed{\Delta G^\circ = -nFE^\circ_{cell}} \quad ...(5.10)$$

Significance of equation (5.10) lies in the fact that it can help in *predicting the feasibility of the cell reaction.* For cell reaction to be spontaneous, ΔG must be **negative,** and for ΔG to be negative, the value of E must be **positive.**

Relationship between Standard EMF and equilibrium constant

We know that standard free energy change is related to equilibrium constant as

$$\Delta G^\circ = -RT \ln K_c$$

also

$$\Delta G^\circ = -nFE^\circ_{cell}$$

$$\therefore \quad nFE^\circ_{cell} = RT \ln K_c = 2.303\, RT \log K_c$$

or

$$E^\circ_{cell} = 2.303 \frac{RT}{nF} \log K_c$$

So we arrive at the same relationship (Eqn. 5.5) by the use of equation (5.10).

Example 5.14. *Calculate the maximum work that can be obtained from the Daniell cell $Zn/Zn^{2+}(aq) \,||\, Cu^{2+}(aq)/Cu$. Given that $E^\circ_{Zn^{2+}/Zn}$ and $E^\circ_{Cu^{2+}/Cu}$ are – 0.76 and + 0.34 V respectively.*

Solution.

Step I. *Calculation of E°_{cell}*

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.34 - (-0.76) = 1.10 \text{ V}$$

Step. II. *Calculation of ΔG°*

We know that maximum work is given by ΔG°.

Now, the net cell reaction is

$$Zn(s) + Cu^{2+}(aq) \longrightarrow Cu(s) + Zn^{2+}(aq)$$

So, here the value of $n = 2$

$$\therefore \quad \Delta G^\circ = -nFE^\circ_{cell}$$
$$= -(2 \text{ mol})(96500 \text{ coul. mol}^{-1})(1.10 \text{ V})$$
$$= -212{,}300 \text{ coul. volts}$$
$$= -212{,}300 \text{ J} = -212.30 \text{ kJ} \quad (\because \text{ Coulomb} \times \text{Volt} = \text{Joule})$$

Example 5.15. *For a cell, $Mg(s)/Mg^{2+}(aq) \,||\, Ag^+(aq)/Ag$ calculate the equilibrium constant at 25°C and also the maximum work that can be obtained by operating the cell.*

$E^\circ_{Mg^{2+}/Mg} = -2.37$ *V and* $E^\circ_{Ag^+/Ag} = +0.08$ *V.* [A.I. (O) CBSE 1991]

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Solution. *Calculation of E°_{cell}*

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= 0.80 - (-2.37) = \mathbf{3.17\ V.}$$

Calculation of ΔG° which gives the maximum work

The cell reaction is : $Mg(s) + 2Ag^+(aq) \longrightarrow 2Ag(s) + Mg^{2+}(aq)$

Thus, value of $n = 2$.

$$\Delta G^\circ = -nFE^\circ_{cell}$$
$$= -2 \times 96500 \times 3.17 = -611810\ C.\ V = \mathbf{-611810\ J.}$$

Calculation of K_c

Now, $$E^\circ_{cell} = \frac{0.059}{n} \log K_c$$

or $$3.17 = \frac{0.059}{2} \log K_c$$

or $$\log K_c = \frac{3.17 \times 2}{0.059} = 107.457$$

$$\mathbf{K_c = 2.864 \times 10^{107}.}$$

Example 5.16. *Given the following cell*

$$Al/Al^{3+}(0.01\ M) \,||\, Fe^{2+}(0.02\ M)/Fe$$

calculate the value of ΔG and E_{cell} at 298 K when $E^\circ_{Al^{3+}/Al}$ and $E^\circ_{Fe^{2+}/Fe}$ are – 1.66 and – 0.44 respectively.

Solution.

Step I. *Calculate of E°_{cell}*

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode} = -0.44 - (-1.66) = 1.22\ V.$$

Step II. *Calculation of E_{cell}*

The net cell reaction is

$$2Al(s) + 3Fe^{2+}(aq) \longrightarrow 2Al^{3+}(aq) + 3Fe(s)$$

Since 6 moles of electrons are involved $\therefore$ $n = 6$.

Now, applying Nernst equation

$$E_{cell} = E^\circ_{cell} + \frac{0.059}{n} \log \frac{[Fe^{2+}]^3}{[Al^{3+}]^2}$$
$$= 1.22 + \frac{0.059}{n} \log \frac{(0.02)^3}{(0.01)^2} = 1.22 + \frac{0.059}{6} \log \frac{(2 \times 10^{-2})^3}{(1 \times 10^{-2})^2}$$
$$= 1.22 + \frac{0.059}{6} \log (8 \times 10^{-2}) = 1.22 + \frac{0.059}{6} (\log 8 - 2)$$
$$= 1.22 + \frac{0.059}{6} (0.9031 - 2) = 1.22 - 0.0197 = \mathbf{1.209\ V.}$$

Step III. *Calculation of ΔG*

Using equation (5.10), we have $\Delta G = -n\ FE_{cell}$

$$= -(6\ mol)(96500\ C\ mol^{-1})(1.209\ V)$$
$$= -700{,}011\ CV = -700{,}011\ J = \mathbf{-700.01\ kJ.}$$

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REVIEW PROBLEMS

5.25. Calculate the free energy change for the cell reaction

$$Zn/Zn^{2+}(4 \times 10^{-4}\ M) \parallel Cd^{2+}(0.2\ M)/Cd.$$

Given that $E^\circ_{Zn^{2+}/Zn} = -0.76$ V and $E^\circ_{Cd^{2+}/Cd} = -0.40$ V.

5.26. Calculate the standard free energy change taking place in H_2/O_2 fuel cell in which the following reactions occur :

(*i*) $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$; $E^\circ = 1.229$ V

(*ii*) $2H_2 \longrightarrow 4H^+ + 4e^-$; $E^\circ = 0.000$ V.

5.27. The zinc-silver oxide cell used in electrical hearing aids has the following reactions :

$$Zn \longrightarrow Zn^{2+} + 2e^- ; \quad E^\circ = 0.76\ V$$

$$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^- ; \quad E^\circ = 0.34\ V$$

Calculate the value of ΔG° in joules.

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5.17. SOME COMMERCIAL CELLS OR BATTERIES

Any cell or battery that we employ as a source of electrical energy is basically an electrochemical cell. The term **battery** is used to represent the *arrangement of two or more galvanic cells connected in series.* Theoretically, the basis of the electrochemical cell is any of the redox reactions. However, in practice the redox reaction used should give the arrangement which fulfills the following requirements :

(*i*) It should be *light* and *compact* ;

(*ii*) Its voltage should not vary appreciably during its use ;

(*iii*) It should provide power for a longer period ; and

(*iv*) It should be rechargeable.

The galvanic cells can be broadly classified into two categories, namely ; *primary cells* and *secondary cells.*

1. **Primary cells.** This type of cells becomes dead over a period of time and the chemical reaction stops. They cannot be recharged or used again. Some common examples are *dry cell, mercury cell,* etc. Let us study the working of a most familiar type of primary cell, the dry cell.

(*a*) **Dry cell.** It is a compact form of *Leclanche cell* known after its discoverer. In this cell, *anode* consists of *zinc container* while *cathode* is a *graphite rod* surrounded by powdered MnO_2 and carbon. The space between the electrodes is filled with the paste of NH_4Cl and $ZnCl_2$. The arrangement is shown in Fig. 5.7.

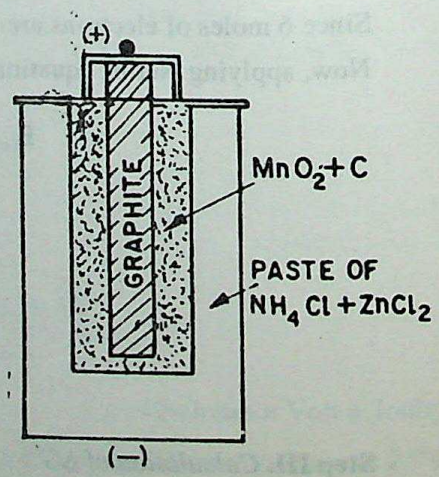

Fig. 5.7. A dry cell.

The reactions taking place at the electrodes are given in their simplified form as follows :

Cathode : $MnO_2 + NH_4^+ + e^- \longrightarrow MnO(OH) + NH_3$

(*Oxidation state of Mn changes from + 4 to + 3*)

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Anode : $Zn \longrightarrow Zn^{2+} + 2e^-$

The zinc ions (Zn^{2+}) so produced combine with ammonia liberated in cathodic reaction to form diammine zinc (II) cation.

$$Zn^{2+} + 2NH_3 \longrightarrow [Zn(NH_3)_2]^{2+}$$

Dry cells do not have long life as NH_4Cl which is acidic, corrodes the zinc container even if the cell is not in use. The cell potential of dry cells lies in the range *1.25 V* to *1.5 V*.

(*b*) **Mercury cell.** It is miniature cell which finds a frequent use these days to supply energy for watches, movie cameras, hearing aids and other compact devices. In mercury cell the *anode* is *zinc-mercury amalgam* and the *cathode* is a paste of *mercury(II) oxide* and *carbon*. Electrolyte is a moist paste of KOH-ZnO. The operating voltage for mercury cell is $\simeq$ 1.30 V and the cell reactions are as follows :

Anode : $\underset{\text{(Amalgam)}}{Zn} + 2OH^- \longrightarrow ZnO(s) + H_2O(l) + 2e^-$

Cathode : $HgO(s) + H_2O(l) + 2e^- \longrightarrow Hg(l) + 2OH^-$

Net reaction : $\underset{\text{(Amalgam)}}{Zn(Hg)} + HgO(s) \longrightarrow ZnO(s) + Hg(l)$

Such a cell shows constancy in its potential throughout its life.

1. **Secondary cells*.** This type of cells can be recharged by passing *direct current* through them and can be used again and again. Some examples are lead-storage battery, nickel-cadmium storage cell, etc. Let us study the working of *lead storage cell.*

(*b*) **Lead-storage battery.** It is the most frequently used battery in automobiles. It consists of six voltaic cells connected in series. In each cell *anode* is made of *spongy lead* and *cathode* is a grid of lead *packed with lead dioxide* (PbO_2). The electrolyte is the aqueous solution of H_2SO_4 which is 38% by mass. The reactions taking place in this type of cell can be represented as :

Anode : $Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$

Cathode : $PbO_2 + SO_4^{2-} + 4H^+ + 2e^- \longrightarrow PbSO_4 + 2H_2O$

Net reaction : $Pb + PbO_2 + 4H^+ + 2SO_4^{2-} \longrightarrow 2PbSO_4 + 2H_2O$

During the working of the cell, the concentration of H_2SO_4 decreases as sulphate ions are consumed to form $PbSO_4$. With the decrease in the concentration of H_2SO_4 the density of the solution also decreases. The condition of the battery can be easily checked by measuring the density of the solution.

To enhance the usefulness of the cell, the anode and cathode plates are arranged in alternating manner and they are separately by sheets of insulating material. The anode and cathode plates are separately connected to each other so as to increase the electrode area in contact with electrolyte solution. This increases current delivering capacity of the cell. The *groups of electrodes* constitute *one cell* as shown in Fig. 5.8. The cells are further connected in series so as to increase the voltage of the battery. In 6 volts battery there are 3 cells and in 12 volts battery there are 6 cells.

Recharging the battery. The battery can be recharged by connecting it to an external source of *direct current*. It reverses the flow of electrons resulting in the deposition of Pb on the anode and PbO_2 on the cathode.

*The discussion of secondary cells is not included in CBSE syllabus.

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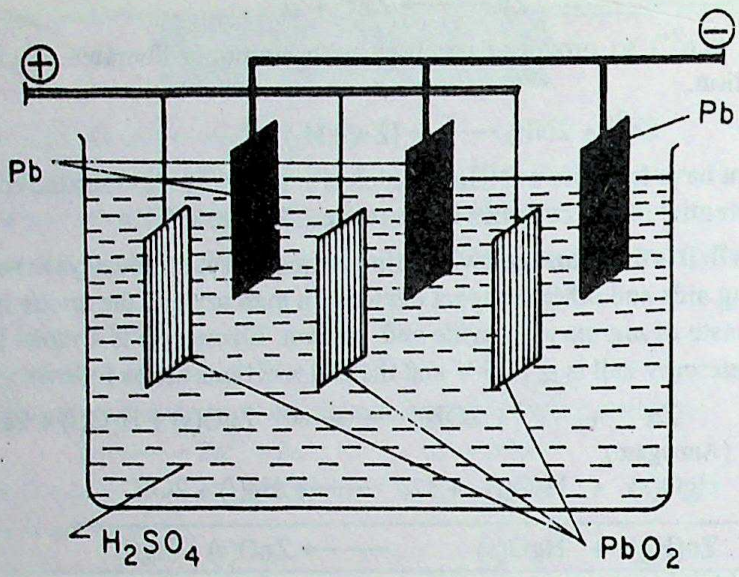

Fig. 5.8. Lead storage cell.

During *recharging* operation the cell behaves as *electrolytic cell*. The recharging reactions are :

Anode : $PbSO_4(s) + 2e^- \longrightarrow Pb(s) + SO_4^{2-}(aq)$

Cathode : $PbSO_4(s) + 2H_2O(l) \longrightarrow PbO_2(s) + SO_4^{2-}(aq) + 4H^+(aq) + 2e^-$

Net : $2PbSO_4(s) + 2H_2O(l) \longrightarrow Pb(s) + PbO_2(s) + 4H^+(aq) + 2SO_4^{2-}(aq)$

Such an operation becomes possible because $PbSO_4$ formed during discharge operation is solid and sticks to the electrodes. Therefore, it is in a position to lose or gain electrons during electrolysis.

(*b*) **Nickel-cadmium storage cell.** It is another rechargeable cell. It consists of *cadmium anode* and the cathode is comprised of a metal grid containing *nickel (IV) oxide*. These are immersed in KOH solution. The reactions occurring are :

Anode : $Cd(s) + 2OH^-(aq) \longrightarrow Cd(OH)_2(s) + 2e^-$

Cathode : $NiO_2(s) + 2H_2O(l) + 2e^- \longrightarrow Ni(OH)_2(s) + 2OH^-(aq)$

Net reaction : $Cd(s) + NiO_2(s) + 2H_2O(l) \longrightarrow Cd(OH)_2(s) + Ni(OH)_2(s)$

The cell is also called ***nicad cell*** and has *voltage* ≈ **1.4 V.**

As is evident, there are no gaseous products, the products formed adhere to the electrodes and can be reconverted by *charging process*. The cell is becoming more popular these days and finds use in electronic watches and calculators.

5.18. FUEL CELLS

In recent years, the scientists have designed the cells which convert chemical energy of a fuel directly into electrical energy. Such cells are called **fuel cells.** These are the voltaic cells in which, the fuels such as H_2, CO, CH_4, C_3H_8, etc., are used to generate electrical energy without the intervention of thermal devices like boiler, turbines, etc.

The conventional method of conversion of chemical energy of a fuel into electrical energy involves combustion of a fuel to liberate heat. The heat energy so produced is used to generate steam for spinning the turbines which are coupled to electrical generators. This process is approximately 40% efficient.

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Fuel cells are designed in such a way that the materials to be oxidised and reduced at the electrodes are stored out side the cell and are constantly supplied to the electrodes. One of the most successful fuel cells uses the reaction of *hydrogen* and *oxygen* to form water and is known as H_2—O_2 fuel cell. The H_2—O_2 fuel cell is also called **Bacon cell** after the name of its inventor and it had been used to power the *Apollo Moon Missions*. The experimental arrangement is shown in Fig. 5.9.

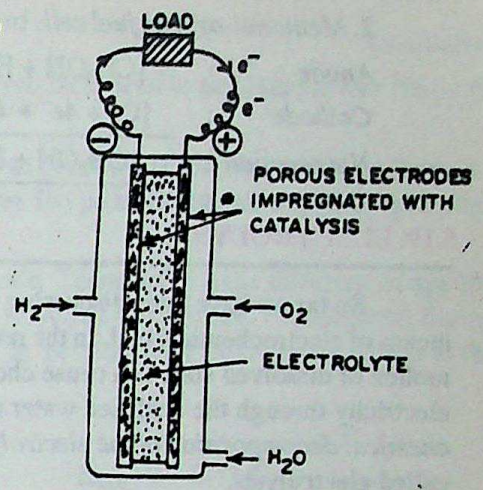

Fig. 5.9. A Single Bacon Cell.

The cell consists of porous carbon electrodes which are impregnated with catalyst (Pt, Ag or CoO). Hydrogen and oxygen are bubbled through the electrodes into electrolyte which is an aqueous solution of NaOH or KOH.

The electrode reactions are :

Anode : $[H_2(g) + 2OH^-(aq) \longrightarrow 2H_2O(l) + 2e^-] \times 2$

Cathode : $O_2(g) + 2H_2O(l) + 4e^- \longrightarrow 4OH^-(aq)$

Net reaction : $2H_2(g) + O_2(g) \longrightarrow 2H_2O(l)$

The cell runs continuously as long as the gases hydrogen and oxygen are supplied at the temperature 525 K and 50 atm. pressure.

Advantages of fuel cells

Some prominent advantages of fuel cells are being described as follows :

1. Pollution free working. There is no harmful or objectionable product formed in fuel cells. Hence they donot cause pollution problems.

2. High efficiency. The efficiency of fuel cells is approximately 70—75%, which is much higher than the conventional cells.

It may be noted that thermodynamic efficiency of fuel cells is the ratio of the electrical free energy to the ΔH of the reaction. For example, for H_2—O_2 fuel cell

$$\eta = \frac{\Delta G}{\Delta H} = \frac{-nFE}{\Delta H} = \frac{-229 \text{ kJ}}{-242 \text{ kJ}}$$

$$= 0.095\% \text{ or } 95\%$$

This theoretical **thermodynamic efficiency,** however, cannot be achieved because of the over potentials at the electrodes.

(*iii*) **Continuous source of energy.** Unlike conventional batteries, energy can be obtained from the fuel cell continuously so long as the supply of fuel is maintained.

The H_2/O_2 cell has been used for generating electrical power in the Apollo space programmes.

Other examples of fuel cells

1. *Propane-oxygen fuel cell.* In C_3H_8—O_2 fuel cell the electrode reactions are :

Anode : $C_3H_8 + 6H_2O \longrightarrow 3CO_2 + 20H^+ + 20e^-$

Cathode : $5O_2 + 20H^+ + 20e^- \longrightarrow 10H_2O$

Net reaction : $C_3H_8 + 5O_2 \longrightarrow 3CO_2 + 4H_2O$

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2. *Methanol-oxygen fuel cell.* In $CH_3OH—O_2$ cell. The electrode reactions involved are

Anode : $[CH_3OH + H_2O \longrightarrow CO_2 + 6H^+ + 6e^-] \times 2$

Cathode : $[O_2 + 4e^- + 4H^+ \longrightarrow 2H_2O] \times 3$

Net reaction : $2CH_3OH + 3O_2 \longrightarrow 2CO_2 + 6H_2O$

5.19. ELECTROLYSIS

So far we have been discussing the process of conversion of chemical energy into electrical energy by means of electrochemical cell. In the reverse process, the passage of electricity through the electrolytes in their molten or dissolved state can cause chemical changes under suitable conditions. For example, the passage of electricity through the acidified water results in the formation of hydrogen and oxygen gases. *The process of chemical decomposition of the electrolyte by the passage of electricity through its molten or dissolved state is* called **electrolysis.**

Electrolytic cell. The device in which the process of electrolysis is carried out is called electrolytic cell. It consists of :

(*i*) *Electrolytic tank*, which is made of some non-conducting material like glass, wood or bakelite.

(*ii*) *Electrolyte* in its dissolved state or molten state.

(*iii*) *Source of electricity* ; an electrochemical cell or battery.

(*iv*) Two *metallic strips rods*, suspended in the electrolyte and connected to the battery through conducting wires. These rods are called *electrodes*. The electrode connected to the negative terminal of battery is called *cathode* while the other one which is connected to the positive terminal is called *anode*. The apparatus used to constitute electrolytic cell has been shown in Fig. 5.10.

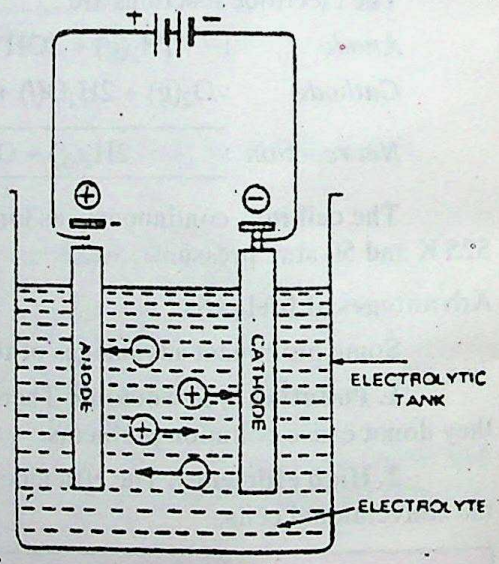

Fig. 5.10. Electrolytic cell.

5.20. CRITERIA OF PRODUCT FORMATION IN ELECTROLYSIS

The process of electrolysis can be explained on the basis of the *theory of ionisation*. When an electrolyte is dissolved in water, it splits up into charged particles called *ions*. The positively charged ions are called cations while the negatively charged ions are called anions. The ions are free to move about in aqueous solution. When electric current is passed through the solution, the ions respond to the applied potential difference and their movement is directed towards the oppositely charged electrodes. The *cations* move towards the *negatively charged electrode* while *anions* move towards the *positively charged electrode*. The formation of products at the respective electrodes is due to **oxidation** (*loss of electrons*) at the **anode** and **reduction** (*gain of electrons*) at the **cathode.**

For example, when electricity is passed through the molten sodium chloride [NaCl(*l*)], sodium is deposited at the cathode while Cl_2 gas is liberated at the anode. The process can be represented as :

$$NaCl(l) \longrightarrow Na^+ + Cl^-$$

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Anode : $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$ (*Oxidation*)

Cathode : $Na^+ + e^- \longrightarrow Na$ (*Reduction*)

Similarly, electrolysis of molten lead bromide [$PbBr_2(l)$] produces lead at the cathode and Br_2 at the anode.

In case there is a possibility of formation of more than one products at the electrodes, or there is a competition between the liberation of ions at the electrodes, then the product formed depends upon their respective electrode potentials, as described below :

(*a*) **At the cathode.** *Reduction process occurs at the cathode.* Therefore, for the different competing reduction processes, the one with *higher reduction potential, will preferably take place.* For example, during the electrolysis of aqueous solution of sodium chloride there is possibility of following reactions at the cathode :

Reduction of Na^+ ions

$$Na^+(aq) + e^- \longrightarrow Na(s)\ ; \qquad E_{Red}^\circ = -2.71\ V$$

and *Reduction of H_2O molecules*

$$H_2O(l) + 2e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)\ ; \qquad E^\circ_{Red} = -0.41\ V$$

Thus, we find that during electrolysis of aqueous solution of NaCl, the reduction of water will preferably take place at the cathode because E°_{red} of water is higher. Hence, the product of electrolysis at the cathode will be H_2 gas instead of $Na(s)$.

Now, let us compare, the E°_{red} values of copper and H_2O.

$$Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)\ ; \qquad E^\circ = 0.34\ V$$

$$H_2O(l) + 2e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)\ ; \qquad E^\circ = -0.41\ V$$

Thus, during electrolysis of aqueous solution of copper sulphate reduction of Cu^{2+} ions will take place at the cathode in preference to the reduction of H_2O molecules.

(*b*) **At the anode.** *Oxidation process occurs at the anode.* Therefore, for different competing oxidation processes, the one with *higher oxidation potential* (or *lower reduction potential) will preferably occur.* For example, if we carry out electrolysis of aqueous solution of copper sulphate, the competing oxidation processes at the anode are :

Oxidation fo SO_4^{2-} ions

$$2SO_4^{2-}(aq) \longrightarrow S_2O_8^{2-} + 2e^-\ ; \qquad E^\circ_{oxi} = -2.01\ V$$

and *Oxidation of water molecules*

$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-\ ; \qquad E^\circ_{oxi} = -1.23\ V$$

As oxidation potential of water is higher, the product formed at the anode will be O_2 gas instead of $S_2O_8^{2-}$ ion.

Similarly, if the electrolysis of copper sulphate solution is carried out using *copper electrodes*, then the process occurring at the anode will be *oxidation of copper atoms to copper* ions instead of oxidation of water because oxidation potential of Cu is higher.

$$Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-\ ; \qquad E^\circ_{oxi} = -0.34\ V$$

$$2H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^-\ ; \qquad E^\circ_{oxi} = -1.23\ V$$

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Thus, in such a case copper from anode will go on dissolving into solution as Cu^{2+} ions while Cu^{2+} ions from solution will go on depositing at the cathode as copper atoms.

The above discussion leads us to a conclusion that for different competing reactions at the electrodes :

Cathodic reaction will be the one with higher E°_{Red} value

Anodic reaction will be the one with higher E°_{Oxi} value

It may be noted that in some cases the **unexpected results** are obtained due to *over voltage**. For example, let us compare the oxidation potentials of Cl^- ion and water

$$H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(aq) + 2e^- ; \qquad E^\circ_{oxi} = -1.23\ V$$

$$Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^- ; \qquad E^\circ_{oxi} = -1.36\ V$$

Although oxidation potential of H_2O is more than that of Cl^- ions, yet during the electrolysis of *concentrated solution of sodium chloride*, the chloride ions oxidise in preference to H_2O molecules at the anode giving Cl_2 gas as the product.

In the light of the above discussion let us discuss the product formed during the electrolysis of some of the electrolytes.

1. Electrolysis of aqueous solution of NaCl. NaCl in aqueous solutions ionises as

$$NaCl(aq) \longrightarrow Na^+(aq) + Cl^-(aq)$$

Reaction at anode : $Cl^-(aq) \longrightarrow \frac{1}{2}Cl_2(g) + e^-$

Reaction at cathode : $H_2O(l) + 2e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-(aq)$

Thus, Cl_2 gas is liberated at the anode whereas H_2 gas is liberated at the cathode.

2. Electrolysis of copper sulphate solution using platinum electrodes. Copper sulphate ionises in aqueous solution

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Reaction at anode : $H_2O(l) \longrightarrow \frac{1}{2}O_2(g) + 2H^+(g) + 2e^-$

Reaction at cathode : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Thus, copper is deposited at the cathode, and O_2 gas is liberated at the anode.

3. Electrolysis of copper sulphate solution using copper electrodes. Copper sulphate ionises as :

$$CuSO_4(aq) \longrightarrow Cu^{2+}(aq) + SO_4^{2-}(aq)$$

Reaction at anode : $Cu(s) \longrightarrow Cu^{2+}(aq) + 2e^-$

Reaction at cathode : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$

Thus, copper dissolves at the anode and is deposited at the cathode.

---

*The transference of electrons from water is *kinetically slow process* as it requires relatively large activation energy. The slowness of electrode reaction creates some electrical resistance at the electrode surface. Hence, extra potential or voltage is required to provide activation energy and to overcome resistance in case of oxidation of water molecules. This extra voltage required for the oxidation of water is called **over voltage.** Due to over voltage, the oxidation of Cl^- ions occurs in preference to H_2O.

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5.21. QUANTITATIVE ASPECT OF ELECTROLYSIS

As pointed out earlier that during electroylsis anodic reaction involves oxidation and cathodic reaction involves reduction. For example, cathodic reaction in electrolysis of copper (II) sulphate is :

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

This means that for the production of one mole of copper, 2 moles of electrons are needed. If the number of electrons available to copper ions are less than 2 moles, the amount of copper deposited at the cathode will also be less than 2 moles. Thus, the amount of product formed at the electrode depends on the number of electrons, which in turn depends on the quantity of electricity flowing through the electrolytic cell

Now charge on one electron has been found to be 1.602×10^{-19} coulombs.

Charge on one mole of electrons $= 1.602 \times 10^{-19} \times 6.02 \times 10^{23} = 96488 \text{ C mol}^{-1}$

This magnitude of charge (= 96488 C mol^{-1}) is called **Faraday constant** and is denoted by **F.** It is in honour of Michael Faraday who discovered laws of electroiysis.

$$F = 96488 \text{ C mol}^{-1} \quad \text{or} \quad \simeq 96500 \text{ C mol}^{-1}.$$

Charge on **n moles** of electrons (Q) is given by **Q = nF**

Thus, for **n** moles of electrons, the charge equal to **nF**, *i.e.*, $n \times 96500$ C has to be passed through the electrolyte. For example, during the electrolysis of aluminium chloride 3 moles of electrons are required for producing 1 mole of aluminium.

$$Al^{3+} + 3e^- \longrightarrow Al$$

Therefore, charge equal to 3 F or 3×96500 C has to be passed through the electrolyte.

Now, quantity of charge flowing through the electrolyte can be calculated from the current strength and time for which the current is passed according to following relation.

$$\mathbf{Q = I \times t}$$

where, **Q** = Quantity of charge (coulombs)

I = Current in amperes

t = time in seconds.

Thus, from the above considerations it is possible to calculate the amount of a substance deposited or evolved (if gas) when a definite amount of current is passed for a definite period of time. It is illustrated in the following examples.

FARADAY'S LAWS OF ELECTROLYSIS

The relationship between the quantity of electricity passed and the quantity of a substance liberated at an electrode is given in the form of Faraday's laws of electrolysis.

Faraday's First Law of Electrolysis

This law states that *the mass of a substance produced at an electrode is directly proportional to the quantity of electricity passed.*

$$m \propto Q$$
$$\propto I \times t$$
$$= Z \times I \times t$$

Here, Q = quantity of electricity

I = current in amperes

t = time in seconds

Z = Electrochemical equivalent

If I = 1 ampere and t = 1 second, then

$m = Z$

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Thus, **electrochemical equivalent** *of a substance is the amount of substance liberated at the electrode when current of one ampere is passed through the electrolyte for one second.*

Faraday's Second Law of Electrolysis

This law states that *when same quantity of electricity is passed through different electrolytes then the masses of the substances liberated at the electrodes are in the ratio of their equivalent masses or their chemical equivalents*

$$\frac{\text{Mass of A}}{\text{Mass of B}} = \frac{E_A}{E_B} = \frac{Z_A}{Z_B}.$$

Example 5.17. *For how long a current of 1.5 ampere has to be passed through the electrolyte in order to deposit 1.0 g of Al when the electrode reaction is*

$$Al^{+3} + 3e^- \longrightarrow Al \text{ (At. mass of Al = 27)}$$

Solution. Step I. *Calculation of number of coulombs required.*

From the electrode reaction, it is clear that

For depositing one mole of Al atoms the electrons required

= 3 mol

Charge on 3 mol of electrons = 3 × 96500 C

Now 1 mol of Al = 27 g

∴ Deposition of 27 g of Al requires charge = 3 × 96500 C

Deposition of 1.0 g of Al requires charge $= \frac{3 \times 96500}{27} \times 1.0 =$ **10722.2 C.** ...(*i*)

Step II. *Calculation of time*

Current strength = 1.5 amp.

Let the time required by *t* sec

∴ No. of coulombs = 1.5 × *t* C ...(*ii*)

Equate (*i*) and (*ii*), 1.5 *t* = 10722.2

$$t = \frac{10722.2}{1.5} = 7148 \text{ sec} = \frac{7148}{60 \times 60} \text{ hrs} = \mathbf{1.98 \text{ hrs.}}$$

Example 5.18. *Calculate the mass of hydrogen evolved by passing a current of 0.5 ampere for 40 minutes through acidified water.*

Solution. Current strength = 0.5 amp.

Time = 40 minutes = 40 × 60 = 2400 sec.

Total quantity of electricity passed = 0.5 × 2400 = 1200 coulombs

Now the electrode reaction is $H^+ + e^- \longrightarrow \frac{1}{2} H_2$

Thus, formation of $\frac{1}{2}$ mol (1.008 g) of hydrogen requires electrons

= 1 mol.

∴ Formation of 1.008 g of H_2 requires charge = 96500 C.

Now 96500 coulombs of electricity produces hydrogen = 1.008 g

1200 coulombs of electricity will produce hydrogen $= \frac{1.008 \times 1200}{96500} =$ **0.0126 g.**

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Example 5.19. *The electrolysis of a metal salt solution was carried out by passing a current of 4 amp for 45 minutes. It resulted in deposition of 2.977 g of a metal. If atomic mass of the metal is 106.4 g mol^{-1}, calculate the charge on the metal cation.*

Solution. Let the charge on the metal ion be $n+$.

∴ The reduction half reaction is

$$\underset{(1\text{ mol})}{M^{n+}} + \underset{(n\text{ mol})}{ne^-} \longrightarrow \underset{(106.4\text{ g})}{M}$$

Quantity of electricity required for depositing 106.4 g of metal

$$= n \times 96500 \text{ C}$$

Quantity of electricity required for depositing 2.977 g of metal

$$= \frac{n \times 96500 \times 2.977}{106.4} = n \times 2700 \text{ C}$$

Quantity of electricity actually passed

$$= 4 \times 45 \times 60 \text{ C} = 10800 \text{ C}$$

Now, $10800 = n \times 2700$

∴ $n = \frac{10800}{2700} = 4$

Hence, charge on metal ion = **+ 4.**

Example 5.20. *Silver is electrodeposited on a metallic vessel of surface area 800 cm^2 by passing a current of 0.2 ampere for 3 hours. Calculate the thickness of the silver deposited. Given the density of silver as 10.47 g/cc (Atomic mass of Ag = 107.92).* (I.I.T. Entrance 1986 ; H.P. Board 1993)

Solution. *Calculation of mass of Ag deposited*

The electrode reaction is : $Ag^+ + e^- \longrightarrow Ag$

The quantity of electricity passed = Current × Time

= 0.2 amp. × 3 × 60 × 60 sec = 2160 C.

From the electrode reaction, it is clear that

96500 C of electricity deposit Ag = 107.92 g

2160 C of electricity deposit Ag $= \frac{107.92}{96500} \times 2160 = 2.42$ g

Calculation of thickness

Let the thickness of deposit be x cm.

∴ Mass = Volume × density

= Area × thickness × density

(Volume = area × thickness)

∴ $2.42 \text{ g} = 800 \text{ cm}^2 \times x \text{ cm} \times 10.47 \text{ g cm}^{-3}$

∴ $x = \frac{2.42}{800 \times 10.47} \text{ cm} = \mathbf{2.89 \times 10^{-4}}$ **cm.**

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REVIEW PROBLEMS

5.28. How many grams of chlorine can be produced by the electrolysis of molten NaCl by a current of 1.00 amp. for 15 minutes ?

5.29. It is required to deposit 0.59 g of copper by the electrolysis of $CuSO_4$ solution by using a current of 0.25 amp. For how long the electrolysis has to be carried out.

5.30. A solution containing Cu^{2+} ions was electrolysed for 30 min. using a current of 3.0 amp., what mass of copper would be deposited ?

5.31. How many coulombs are required to produce :

(*i*) 20.0 g of calcium form molten $CaCl_2$.

(*ii*) 50.0 g of aluminium form molten Al_2O_3.

5.32. A solution of $Ni(NO_3)_2$ is electrolysed between platinum electrodes using a current of 5.0 ampere for 30 minutes. What mass of Ni will be produced at the cathode ? (At. mass of Ni = 58.70).

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Difference between Electrochemical Cell and Electrolytic Cell

We have learnt that there are two types of cells namely : *electrochemical cells* and *electrolytic cells*. The former is a device which converts chemical energy into electrical energy. On the other hand, electrolytic cell is a device which converts electrical energy into chemical energy. The two cells also differ significantly with respect to the charges on the electrodes. For example, in electrochemical cell anode is negative whereas in electrolytic cell, the anode is positive. Similarly, cathode is positive in electrochemical cell whereas it is negative in the electrolytic cell. The main points of difference have been summed up as follows in Table 5.6.

Table 5.6. Differences between Galvanic Cell and Electrolytic Cell

Galvanic cell	*Electrolytic cell*
1. In galvanic cell, electrical energy is produced.	1. In electrolytic cell, electrical energy is consumed.
2. In galvanic cell, reaction taking place is spontaneous.	2. In electrolytic cell, reaction taking place is non-spontaneous.
3. The two half cells are set up in different containers and are connected through salt bridge or porous partition.	3. Both the electrodes are placed in the solution or molten electrolyte in the same container.
4. In galvanic cell, anode is negative and cathode is positive.	4. In electrolytic cell, the anode is positive and cathode is negative.
5. The electrons move from anode to cathode in external circuit.	5. The electrons are supplied by the external source. They enter through cathode and come out through anode.

5.22. CORROSION

It is a matter of common observation that certain metals (except those which are least reactive like Au, Pt, Pd etc.) are slowly eaten up on long exposure to atmophere. For example :

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silver gets tarnished,
copper develops green coating on its surface,
iron rusts, and
lead loses its lustre.

In fact, such metals react with the gases or moisture present in the environment to form undersirable compounds. This process in general is referred to as *corrosion*. **Corrosion** may, thus, be defined as

the process of slow conversion of metals into their undesirable compounds (usually oxides) by reaction with moisture and other gases present in the atmosphere.

Factors Which Affect Corrosion

The factors which affect the rate of corrosion are :

(*i*) **Reactivity of the metal.** The more active metals are more prone to corrosion.

(*ii*) **Presence of impurities.** Presence of impurities helps in setting up a corrosion cell and makes the corrosion to occur rapidly. For example, pure iron does not rust.

(*iii*) **Air and moisture.** Air and moisture are quite helpful in corrosion. The presence of gases like CO_2 and SO_2 in air makes it still rapid. For example, no rusting is caused if iron is kept in vacuum.

(*iv*) **Strains in metal.** Strains in metal also help in corrosion. For example, in iron articles, rusting is more pronounced on the areas having bends, dents, scratches, nicks and cuts.

(*v*) **Presence of electrolytes.** The presence of electrolytes also makes the corrosion process faster. For example, iron rusts more rapidly in saline water in comparison to pure water.

Let us understand the **mechanism of corrosion** by studying the most familiar example of **rusting of iron.** Chemically rust is hydrated iron (III) oxide, $Fe_2O_3 . xH_2O$. It is generally caused by moisture, CO_2, O_2 of air. Rust is a non-sticking brown-coloured material which can be easily removed by scratching. There are a number of theories about the mechanism of rusting. The most widely accepted theory *i.e., electrochemical theory* is being discussed here.

Electrochemical Theory of Rusting

According to this theory, the *impure iron* surface behaves like a small electrochemical cell in presence of water containing dissolved oxygen or carbon dioxide. Such a cell is also called *corrosion cell* or *corrosion couple*. In these miniature corrosion cells, pure iron acts as anode and impure surfaces act as cathode. Moisture having dissolved oxygen or carbon dioxide in it constitutes electrolytic solution.

At anode, oxidation of Fe atoms takes place. Thus, Fe atoms pass into solution as Fe^{2+} ions leaving behind electrons in the metal which are pushed into cathodic area.

$$Fe \longrightarrow Fe^{+2} + 2e^- ; E^\circ_{oxi} = -0.44 \text{ V} \quad ...(1)$$

At cathode, the electrons are picked up by the H^+ ions which are produced either from H_2O or from H_2CO_3 (formed by dissolution of CO_2 in moisture).

$$CO_2 + H_2O \longrightarrow H^+ + HCO_3^-$$

$$2H^+(aq) + 2e^- \longrightarrow 2H$$

The H atoms, thus, formed, reduce the dissolved oxygen as

$$2H + \tfrac{1}{2}O_2 \longrightarrow H_2O$$

The net reduction process at the *cathodic area* is

$$2H^+ + \tfrac{1}{2}O_2 + 2e^- \longrightarrow H_2O ; E^\circ_{Red} = 1.23 \text{ V} \quad ...(2)$$

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$$2Fe^{2+} + \frac{1}{2}O_2 + (2+x)H_2O \longrightarrow Fe_2O_3 . xH_2O + 4H^+$$

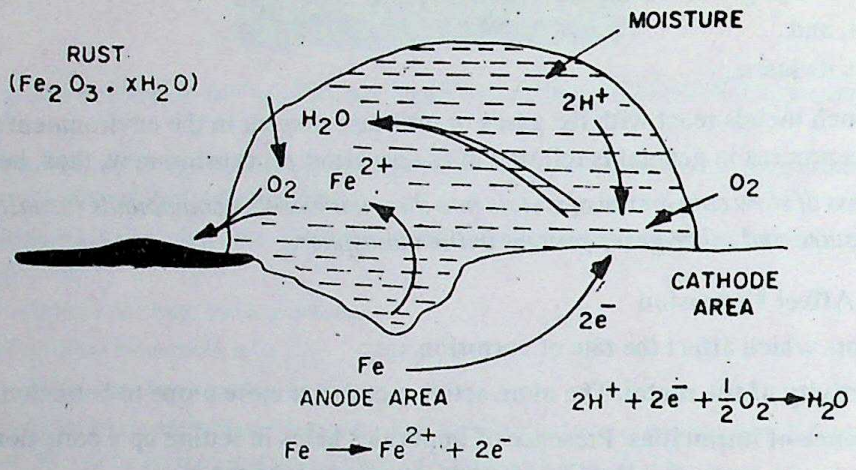

Fig. 5.11. Rusting of iron.

The net reaction of the corrosion cell can be put as

$$Fe + 2H^+ + \frac{1}{2}O_2 \longrightarrow Fe^{2+} + H_2O \; ; E^\circ_{cell} = 1.67 \text{ V}$$

The ferrous ions so formed move through water and come at the surface of iron object where these are further oxidised to *ferric state* by atmospheric oxygen and constitute rust which is hydrated iron (III) oxide.

$$2Fe^{2+} + \frac{1}{2}O_2 + 2H_2O \longrightarrow Fe_2O_3 + 4H^+$$

$$Fe_2O_3 + xH_2O \longrightarrow \underset{\text{(Rust)}}{Fe_2O_3.xH_2O}$$

5.23. PREVENTION OF CORROSION

There are several methods for protecting metals from corrosion (iron from rusting). Some of these methods are being discussed as follows :

1. Barrier protection. In this method, a barrier film is introduced between iron and atmospheric oxygen and moisture. Barrier protection can be achieved by any of the following methods :

(*i*) *by painting the surface.*

(*ii*) *by coating the surface with a thin film of oil or grease.*

(*iii*) *by electroplating iron with some non-corrosive metal such as nickel, chromium, copper, etc.*

In this type of protection, if scratches or cracks appear in the protective layer then surface of iron may get exposed. In this region, moisture and oxygen may come in contact with iron and rusting starts. This rusting extends beneath the protective layer and eventually peels off the protective layer.

2. Sacrificial protection. In this method, surface of iron is covered with a layer of *more active metal* like zinc. This active metal loses electrons in preference to iron and hence, prevents the rusting of iron. However, the covering metal gets consumed in due course of time, but so long as it is present, even the nearly uncovered surfaces of iron do not get rusted. In this way, scratches in the protective layer of this type are not harmful. This type of protection is called **sacrificial protection.**

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Zinc metal is generally used for protecting iron and the process is called **galvanization.** Galvanized iron sheets maintain their shine due to the formation of a thin protective layer of basic zinc carbonate, $ZnCO_3.Zn(OH)_2$ due to the reaction between zinc, oxygen, CO_2 and moisture in air.

Zinc, magnesium and aluminium powders dissolved in paints can also be applied as protective layers. The well known aluminium paint contains aluminium powder suspended in varnish.

3. Electrical protection. This is also a case of sacrificial protection. In this method, the exposed surface of iron is protected by connecting it to some more active metal such as magnesium. The other metals which can be used for this purpose are aluminium, zinc, etc. The more active metal acts as anode and loses electrons in preference to iron. The iron surface, acts as cathode. This method, therefore, is also called **cathodic protection** of iron. Underground water pipes or tanks made of iron are protected by connecting them to more easily oxidisable metal as shown in Fig. 5.12.

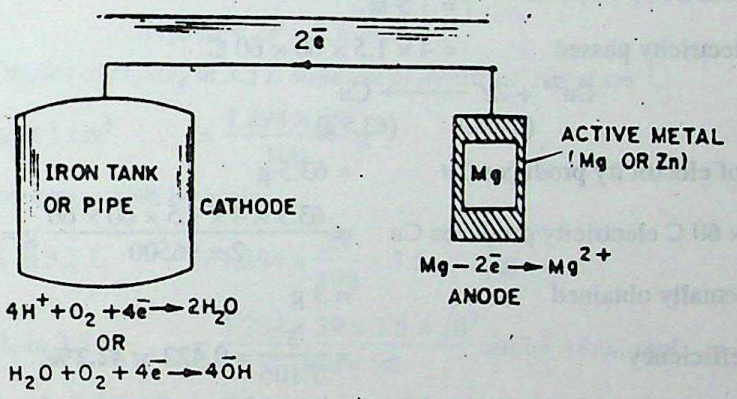

Fig. 5.12. Protection of underground pipe or tank.

4. Use of anti-rust solutions. The alkaline solutions of some phosphate and chromate salts act as anti-rust soluitons. For example, when iron articles are dipped into the boiling and strongly alkaline solution of sodium phosphate, a protective insoluble film of iron phosphate is formed on them. This film protects the articles from rusting. The alkaline nature of solutions prevens the availability of H^+ ions which facilitate the oxidation of iron to Fe^{2+}.

SOME MISCELLANEOUS NUMERICAL PROBLEMS

Example 5.21. *The standard reduction potential of the reation :*

$$2H_2O + 2e^- \rightleftharpoons H_2(g) + 2OH^- \text{ is } -0.8277\ V$$

Calculate equilibrium constant for the reaction

$$2H_2O \rightleftharpoons H_3O^+ + OH^- \text{ at } 25°C.$$ (I.I.T. J.E.E. 1989)

Solution. Consider the given reaction as the net cell reaction. Let us split it into two half cell reactions.

Oxidation half : $H_2O + \frac{1}{2}H_2(g) \longrightarrow H_3O^+ + e^-$; $E°_{oxi} = 0.00$ V ...(1)

(it refers to SHE)

Reduction half : $H_2O + e^- \longrightarrow \frac{1}{2}H_2(g) + OH^-$; $E°_{Red} = -0.8277$ ...(2)

Add the two to get the net reaction.

Net cell reaction : $2H_2O \rightleftharpoons H_3O^+ + OH^-$; $E°_{cell} = -0.8277$

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It is evident from the cell reaction that it involves the transfer of *one* e^- so that $n = 1$.

Now, $$\log K_c = \frac{n}{0.059} E^\circ_{cell} = \frac{1}{0.059}(-0.8277) = -14.028 = \overline{15}.972$$

$$K_c = \text{antilog}\,(\overline{15}.972) = \mathbf{9.376 \times 10^{-15}}.$$

Example 5.22. *A current of 4 amp was passed for 1.5 hours through a solution of copper sulphate when 3.0 g of copper was deposited. Calculate the current efficiency.*

Solution. The current efficiency is given by the relation

Current efficiency $$= \frac{\text{Mass of metal actually deposited}}{\text{Theoretical mass that can be deposited}}$$

Calculation of theoretical mass I = 4 amp

t = 1.5 hr.

Quantity of electricity passed $= 4 \times 1.5 \times 60 \times 60$ C

$$Cu^{2+} + 2e^- \longrightarrow Cu$$
(2 mol) (63.5 g)

2×96500 C of electricity produces Cu = 63.5 g

$4 \times 1.5 \times 60 \times 60$ C electricity produces Cu $= \dfrac{63.5 \times 4 \times 1.5 \times 60 \times 60}{2 \times 96500}$ g = 7.106 g

Mass of Cu actually obtained = 3 g

∴ Current efficiency $= \dfrac{3}{7.106} = 0.422$ or **42.2%.**

Example 5.23. *A current of 1.70 amp was passed through 300 ml of 0.160 M solution of $ZnSO_4$ for 230 sec with a current efficiency of 90%. Find the molarity of zinc (Zn^{+2}) after the deposition of zinc. Assume that volume of solution remains constant during electrolysis.* (I.I.T. J.E.E. 1991)

Solution. *Calculation of theoretical amount of zinc*

Quantity of electricity = 1.70 A × 230 sec = 391 C

The electrode reaction is $$Zn^{2+} + 2e^- \longrightarrow Zn$$
(2 mol) (1 mol)

2×96500 C of electricity produces Zn = 1 mol

391 C of electricity produces Zn $= \dfrac{391}{2 \times 96500}$ mol = 0.0020 mol

Since current efficiency is 90%

∴ Amount of Zn actually deposited $= \dfrac{0.0020}{100} \times 90 = 0.0018$ mol

Amount of Zn^{2+} ions initially present in solution

$= V_{(mL)} \times M \times 10^{-3}$ mol

$= 300 \times 0.160 \times 10^{-3}$ mol = 0.048 mol

Amount of Zn^{2+} ion left after deposition in 300 ml of solution

= 0.048 − 0.0018 = 0.0462 mol

Molarity of Zn^{2+} after deposition $= \dfrac{0.0462}{300} \times 1000 = \mathbf{0.154\ M.}$

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Example 5.24. *During the discharge of lead storage battery the density of sulphuric acid fell from 1.294 to 1.139 g cm^{-3}. The sulphuric acid of density 1.294 g cm^{-3} is 39% H_2SO_4 by mass and that of density 1.139 g cm^{-3} is 20% by mass. The battery holds 3.5 L of acid and the volume remains practically constant during discharge. Calculate the no. of ampere-hours for which battery must have been used.*

(I.I.T. J.E.E. 1986)

Solution. The electrode reactions of lead storage battery are

$$Pb + SO_4^{2-} \longrightarrow PbSO_4 + 2e^-$$

$$PbO_2 + 4H^+ + SO_4^{2-} + 2e^- \longrightarrow PbSO_4 + 2H_2O$$

Net reaction :

$$Pb + PbO_2 + 2H_2SO_4 \longrightarrow 2PbSO_4 + 2H_2O$$

Thus, it is evident that 2 mol of e^- are transferred for the consumption of 2 mol of H_2SO_4.

Hence, $2H_2SO_4 = 2F = 2 \times 96500$ C. ...(*i*)

Calculation of moles of H_2SO_4 in 3.5 L solution of density 1.294 g cm^{-3}.

Mass of H_2SO_4 in 1 cm^3 $= \dfrac{1.294 \times 39}{100}$ g

(*Here, concentration is 39% by mass*)

Mass of H_2SO_4 in 3.5 L $= 1.294 \times \dfrac{39}{100} \times 3.5 \times 10^3$ g

Moles of H_2SO_4 in 3.5 L $= \dfrac{1.294 \times 39 \times 3.5 \times 10^3}{100 \times 98}$ mol = 18.02 mol.

Calculation of moles of H_2SO_4 in 3.5 L solution of density 1.139 g cm^{-3}.

(Here concentration is 20% by mass)

Moss of H_2SO_4 in 3.5 L $= \dfrac{1\,139 \times 20 \times 3.5 \times 10^3}{100}$ g

Moles of H_2SO_4 in 3.5 L $= \dfrac{1.139 \times 20 \times 3.5 \times 10^3}{100 \times 98}$ mol = 8.135 mol

Moles of H_2SO_4 consumed during discharge = 18.02 – 8.135 = 9.885 mol

Now, 2 mol of H_2SO_4 $= 2 \times 96500$ C

9.885 mol of H_2SO_4 $= \dfrac{2 \times 96500}{2} \times 9.885$ C

Conversion of Coulombs into ampere hour

3600 C = 1 amp-hour

$$\frac{2 \times 96500 \times 9.885}{2} \text{ C} = \frac{2 \times 96500 \times 9.885}{2 \times 3600} \text{ amp-hour}$$

= 264.97 amp-hour.

Example 5.25. *Zinc granules are added in excess to a 500 ml of 1.0 M nickel nitrate solution at 25°C until the equilibrium is reached. If the standard reduction potential of Zn^{2+}/Zn and Ni^{2+}/Ni are – 0.75 V and – 0.24 V respectively, find out concentration of Ni^{2+} in solution at equilibrium.* (I.I.T. J.E.E. 1991)

Solution. The relationship between E°_{cell} and K_c is given as

$$E^\circ_{cell} = \frac{0.059}{n} \log K_c \quad ...(1)$$

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Now the redox reaction between Zn and Ni^{2+} can be written as

$$Zn + Ni^{2+} \rightleftharpoons Zn^{2+} + Ni$$

The value of $n = 2$

$$E^\circ_{cell} = E^\circ_{cathode} - E^\circ_{anode}$$
$$= -0.24 - (-0.75) = 0.51 \text{ V}$$

Substituting these values in equation (1), we have

$$0.51 = \frac{0.059}{2} \log K_c$$

$$\log K_c = \frac{2 \times 0.51}{0.059} = 17.288$$

$$K_c = \text{antilog } (17.288) = 1.946 \times 10^{17}$$

Let x moles of Ni^{2+} react at equilibrium

	Zn + Ni^{2+}	$\rightleftharpoons$ Ni + Zn^{2+}
Initial mols :	0.5 mol	
Equilibrium mols :	$(0.5 - x)$ mol	x mol
Equilibrium conc. :	$2(0.5 - x)$ mol L^{-1}	$2x$ mol L^{-1}
	$(1 - 2x)$ mol L^{-1}	$2x$ mol L^{-1}

Now $$K_c = \frac{[Zn^{2+}]}{[Ni^{2+}]} \qquad [\because [Zn] = [Ni] = 1]$$

$$= \frac{2x}{1 - 2x}$$

$\therefore$ $$K_c(1 - 2x) = 2x$$

or $$(1 + K_c)\, 2x = K_c \quad \text{or} \quad 2x = \frac{K_c}{1 + K_c}$$

Now conc. of Ni^{2+} $$= (1 - 2x) = 1 - \frac{K_c}{1 + K_c} = \frac{1 + K_c - K_c}{1 + K_c} = \frac{1}{1 + K_c}$$

Since K_c is very large $\therefore$ $1 + K_c \approx K_c$.

$\therefore$ Conc. of Ni^{2+} $$= \frac{1}{K_c} = \frac{1}{1.946 \times 10^{17}} = 0.5138 \times 10^{-17} = \mathbf{5.138 \times 10^{-18}}.$$

Example 5.26. *Calculate the minimum voltage to cause the electrolysis of a solution of copper nitrate under standard conditions. Given that $E^\circ_{Cu^{2+}/Cu} = 0.34$ V and $E^\circ_{H_2O/H^+} = -1.23$ V.*

Solution. The electrode reactions during the electrolysis of copper nitrate are

Anodic reaction : $Cu^{2+}(aq) + 2e^- \longrightarrow Cu(s)$; $E^\circ_{Red} = 0.34$ V

Cathodic reaction : $H_2O(l) \longrightarrow 2H^+(aq) + \frac{1}{2} O_2(g) + 2e^-$; $E^\circ_{oxi} = -1.23$ V

Net reaction : $Cu^{+2}(aq) + H_2O(l) \longrightarrow 2Cu(s) + \frac{1}{2} O_2(g) + 2H^+(aq)$; $E^\circ_{cell} = -0.89$ V

Thus, minimum voltage required to cause electrolysis is 0.89 V.

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Example 5.27. *The standard reduction potential for the half cell*

$$NO_3^- + 2H^+ + e^- \longrightarrow NO_2(g) + H_2O \text{ is } 0.78 \text{ V}$$

(i) Calculate the reduction potential in 8 M H^+ solution.

(ii) What will be the reduction potential of the half cell in a neutral solution ? Assume other species to be at unit concentration. (I.I.T. J.E.E. 1993)

Solution. The given half cell is

$$NO_3^-(aq) + 2H^+(aq) + e^- \longrightarrow NO_2(g) + H_2O(l)$$

According to Nernst equation

$$E = E^\circ + \frac{0.059}{1} \log \frac{[NO_3^-][H^+]^2}{[NO_2]}$$

(i) Electrode potential at 8M H^+ solution

$$[NO_3^-] = [NO_2] = 1 \quad \text{(As per given conditions)}$$

$$[H^+] = 8 \text{ M}$$

$$\therefore \quad E = 0.78 + \frac{0.059}{1} \log (8)^2 = 0.78 + 0.059 \log 64$$

$$= 0.78 + (0.059)(1.8062) = \mathbf{0.886\ V}$$

(ii) Electrode potential in neutral solution

In neutral solution, $[H^+] = 1 \times 10^{-7}$

$$\therefore \quad E = 0.78 + \frac{0.059}{1} \log (1 \times 10^{-7})^2$$

$$= 0.78 + 0.059 \log (1 \times 10^{-14}) = 0.78 + 0.059 \times (-14)$$

$$= 0.78 - (0.826) = \mathbf{-0.046\ V.}$$

Example 5.28. *Given that standard potentials of Cu^{2+}/Cu and Cu^+/Cu couples as 0.34 V and 0.52 V respectively, calculate the standard electrode potential of Cu^{2+}/Cu^+ couple.*

Solution. It is important to mole that E° values of the two given couples cannot be added directly as these are not extensive properties. Hence it is neccessary to convert E° values into ΔG° values, which can be added or subtracted

$$Cu^{2+} + 2e^- \longrightarrow Cu; \qquad \Delta G_1^\circ = -nFE_1^\circ = -2F \times 0.34 \text{ V} = (-0.68 \text{ F})$$

$$Cu^+ + e^- \longrightarrow Cu; \qquad \Delta G_2^\circ = -nFE_2^\circ = -F \times (0.52 \text{ V}) = -0.52 \text{ F}$$

The required reaction is $Cu^{2+} + e \longrightarrow Cu^+$

Let E° be the standard electrode potential

$$\therefore \quad \Delta G_3^\circ = -nFE^\circ = -FE^\circ$$

Now $\quad \Delta G_3^\circ = \Delta G_2^\circ - \Delta G_1^\circ$

or $\quad -FE^\circ = -0.68 \text{ F} - (-0.52 \text{ F}) = -0.16 \text{ F}$

or $\quad E^\circ = \mathbf{0.16\ V.}$

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IMPORTANT TERMS CONCEPTS AND FORMULAE

- **Electrolyte.** A substance that dissociates in solution to produce ions and hence conducts electricity in dissolved state or molten state.
- **Ohms law.** $\frac{V}{I} = R$
- **Specific Conductance (k).** Conductance of one centimetre cube of a conductor. Its units are $ohm^{-1}\ cm^{-1}$ or $S\ cm^{-1}$.
- **Equivalent Conductance.** Conductance of a solution containing one gram equivalent of the electrolyte, placed between two parallel electrodes one cm apart.

$$\Lambda_{eq} = \frac{1000 \times k}{N}$$

- **Molar Conductance.** Conductance of a solution containing one mole of the electrolyte, placed between two parallel electrodes one cm apart.

$$\Lambda_m = \frac{1000 \times k}{M}$$

- **Conductivity** $= \frac{\text{Cell constant}}{\text{Resistance}} = \text{Cell constant} \times \text{Conductance}$
- Molar conductance of an electrolyte increases with dilution.
- **Kohlrausch's Law.** The molar conductivity of an electrolyte at infinite dilution is equal to the sum of of the conductivities of the individual ions.

$$\Lambda_m^\infty = \nu_+\lambda_+^\infty + \nu_-\lambda_-^\infty$$

- **Degree of dissociation** (α). Fraction of molecules that dissociates in solution.

$$\alpha = \frac{\Lambda_m^c}{\Lambda_m^\infty}$$

- **Ionic Mobility.** It is the distance travelled by the ion per second under the potential gradient of 1 volt-per cm.
- **Potential gradient.** It is the ratio of the potential applied across the electrodes to the distance between the electrodes.
- **Electrochemical Cell.** A device that converts chemical energy into electrical energy.
- **Anode.** In electrochemical cells, the anode is the electrode at which oxidation takes place. It is the negative electrode.
- **Cathode.** In electrochemical cells, the cathode is the electrode at which reduction takes place. It is the positive electrode.
- **EMF** $= E_{cathode} - E_{anode}$
- **Thermodynamic efficiency of cell.** It is the ratio of the electrical free energy to the enthalpy change of the cell reaction.
- **Electrochemical Series.** Arrangement of all the electrodes in the increasing order of their reduction potentials.
- **Nernst Equation.**

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} + \frac{2.303\ RT}{nF} \log \frac{[M^{n+}]}{[M]}$$

or

$$E_{M^{n+}/M} = E^\circ_{M^{n+}/M} + \frac{0.059}{n} \log \frac{[M^{n+}]}{[M]}$$

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- $$E^\circ_{cell} = \frac{0.059}{n} \log K_c$$
- $\Delta G = -nFE_{cell}$
- **Fuel Cell.** A device which converts chemical energy of a fuel directly into electrical energy.
- **Rust.** $Fe_2O_3 . xH_2O$.
- **Electrolysis.** The process of decomposition of electrolyte as a result of passage of electricity through its aqueous solution or through its molten state.
- **Current efficiency.** It is the ratio of the mass of the products actually librated at the electrode to the theoretical mass that could be obtained.

EXERCISE

VERY SHORT ANSWER QUESTIONS
(1 mark)

1. How many Faradays of electricity are required to convert 1 mole of $C_6H_5NO_2$ to $C_6H_5NH_2$?
2. What is equivalent conductivity of 1 M H_2SO_4 solution if its conductivity is 26×10^{-2} ohm^{-1} cm^{-1} ? ***(CBSE 1991)***
3. Can we store copper sulphate solution in iron vessel ?
4. If we carry out the electrolysis of fused calcium hydride what product will form at anode ?
5. Write the chemical formula of rust.
6. Which electrolyte is used in fuel cell ? What is the relation which expresses thermodynamic efficiency of cell ?
7. The thermodynamic efficiency of H_2—O_2 fuel cell is ..... .
8. What is schematic representation of a cell with following overall reaction ?

$$H_2 + Cu^{2+} \longrightarrow 2H^+ + Cu \text{ and e.m.f.} = 0.34 \text{ V.}$$

$$E^\circ_{Cu^{2+}/Cu} = 0.34 \text{ V.}$$

9. Fill in the blanks

1 Faraday = ... C = ... electrons.

10. Can we use a copper vessel to store 1 M $AgNO_3$ solution ? Given that

$$E^\circ_{Cu^{2+}/Cu} = +0.34 \text{ V and } E^\circ_{Ag^+/Ag} = 0.80 \text{ V.}$$ ***[Har (Sc.) 1992]***

11. Do we get same products during electrolysis of molten NaCl and aqueous NaCl ?
12. Can we use voltmeter for determining the EMF of the electrochemical cell ?
13. What should be the sign of ΔG for electrolytic cell reactions ?
14. Suggest the cathodic and anodic reactions for propane-oxygen fuel cell.
15. Why salt-bridge is not required in a lead storage cell ?
16. What is the effect of temperature on the electrical conductance of an electrolytic conductor ?
17. What are the units of equivalent conductivity and molar conductivity ?
18. What is the relationship between specific conductance and molar conductivity ?
19. What is the effect of dilution on equivalent conductivity ?
20. What is the unit of cell constant ?
21. How is the cell conductance related to the specific conductance of the electrolyte ?

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22. What is the relationship between standard EMF and equilibrium constant ?
23. What is a fuel cell ?
24. Why is it not possible to determine the absolute value of electrode potential of an electrode ?
25. What is EMF of the cell ? *(Haryana Board 1993)*
26. Define electrochemical series. *(H.P. Board 1994)*
27. What is the effect of decreasing concentration on the molar conductivity of a weak electrolyte ?
28. How can you increase the reduction potential of an electrode ?
29. What is the standard EMF of NHE ?
30. Write Nernst equation.
31. What is the relationship between ΔG and EMF of a cell ?
32. What is the reaction taking place at anode during electrolysis of $AgNO_3(aq)$ using platinum electrodes ?
33. What are the reactions taking place at anode and cathode in H_2— O_2 fuel cell ?
34. Write down the cell reaction for the cell given below :

$$Cu \mid Cu^{2+}(aq) \parallel Ag^{+}(aq) \mid Ag$$

35. Define corrosion what is the chemical formula of rust ? *(Haryana Board 1996)*
36. Why is it not possible to measure the voltage of an isolated reduction half reaction ? *(Haryana Board 1995)*
37. What is the effect of decreasing concentration on the molar conductivity of a weak electrolyte ? *(A.I. CBSE 1994)*
38. What is the charge on one mole electrons ?
39. What is the effect of temperature on molar conductivity ?
40. Why does a dry cell become dead after a long time even if it has not been used ?

DESCRIPTIVE QUESTIONS
(2—3 Marks)

Conductance, Conductivity and Molar Conductivity

41. Explain the terms :
    (*i*) Conductivity, (*ii*) Molar conductivity, (*iii*) Equivalent conductivity.
    Give units in each case.
42. How is molar conductivity related to the molarity of electrolytic solution ?
43. Define the terms strong and weak electrolytes. How can you differentiate these on the basis of molar conductivity ?
44. How do you account for the increase in the values of molar conductivity with dilution in case of strong and weak electrolytes ?
45. Describe a method to measure electrolytic conductivity.
46. Explain the term cell constant.
47. Differentiate between metallic conductors and electrolytic conductors.
48. State and explain Kohlrausch's law.
49. How can you use Kohlrausch's law for the determination of Λ_m^{∞} for acetic acid ?
50. How can degree of ionisation of weak electrolyte be determined on the basis of Kohlrausch's law ?
51. (*a*) How does molar conductivity of weak electrolyte vary with concentration in solution ? *(CBSE 1993)*
    (*b*) How does molar conductivity of strong electrolyte vary with concentration in solution ? *(CBSE 1993)*
52. Define molar conductivity of an electrolytic solution. Mention the effect of temperature on molar conductivity. *(CBSE 1995)*

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Electrochemical Cells and E.M.F.

53. What is meant by the term Electrochemical Cell ? How does it differ from electrolytic cell ?
54. Explain the working of the galvanic cell by taking the example of $Zn/CuSO_4$ reaction. Also explain the function of the salt bridge.
55. Explain the term electrode potential. How is it related to the temperature and concentration of electrolyte ?
56. Depict the electrochemical cell in which the cell reaction is

$$Zn(s) + 2Ag^+(aq) \longrightarrow Zn^{2+}(aq) + 2Ag(s).$$

Also give

(*a*) anode and cathode reactions (*b*) direction of electrons and also of conventional current

(*c*) positive and negative terminals.

57. What is electrode potential ? How does it arise when a metallic strip is brought in contact with the solution of its own ions ?
58. Why is it not possible to measure the absolute electrode potential of the single electrode ? ***(H.P. Board 1993)***
59. What is the meaning of the statement that $E°_{oxi}$ of zinc is + 0.76 V while $E°_{Red}$ of Ag is + 0.80 V ?
60. What is meant by the abbreviation SHE ? Give its utility.
61. What is standard electrode potential ? How is it denoted ?
62. Write Nernst equation. Use the equation to derive the expression for the cell potential of the following cell :

$$Al/Al^{3+}(aq) \,||\, Cu^{2+}(aq)/Cu.$$

63. Consider the following equations :

$$Au^{3+}(aq) + 3e^- \longrightarrow Au(s); \qquad E°_{Red} = 1.50 \text{ V}$$

$$AuCl_4^- + 3e^- \longrightarrow Au(s) + 4Cl^-; \qquad E°_{Red} = 1.00 \text{ V}$$

(*a*) Which of these species is best oxidising agent ?

(*b*) Could Au be plated better from an aqueous solution of $AuCl_3$ or from $NaAuCl_4$ and why ?

(*c*) At which electrode would gold be deposited ?

64. In a copper-zinc cell what would be the effect on cell voltage, if

(*a*) SO_4^{2-} ions are added to Cu^{2+} ion compartment

(*b*) $CuSO_4$ solution is added to Cu^{2+} ion compartment

(*c*) SO_4^{2-} ion, in excess are added to Zn^{2+} ion compartment

(*d*) The size of the zinc electrode were increased.

65. What is meant by standard e.m.f. of the cell ? Derive the expression between standard e.m.f. of the cell and equilibrium constant.
66. What is free energy and free energy change ? How is free energy change related to cell potential ? Explain.
67. Describe giving the anode and cathode reactions, the construction of *dry cell.*
68. Why does a cell stop working and becomes dead over a period of time ?
69. Give chemical reactions taking place during charging and discharging operation of lead storage-battery.
70. In what respects do primary cells differ from the secondary cells ?
71. What are Fuel Cells ? Describe giving diagram the working of H_2— O_2 cell. ***(P.S.E.B. 1992)***
72. What advantages do fuel cells have over conventional methods of generating electrical energy ?
73. What are the chemical reactions of mercury cell ? Why its voltage remains constant throughout its life span ?
74. What are fuel cells ? Write the reactions of an oxygen-hydrogen fuel cell. ***(A.I. CBSE 1994)***
75. Arrange the following metals in order in which they displace each other. Use the values of $E°_{Red}$ from the table.

Al, Cu, Fe, Mg, Zn.

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76. Electrode potentials of the metals in their respective solutions are provided. Arrange the metals in their increasing order of reducing power,

$$K^+/K = -2.93\ V\ Ag^+/Ag = +0.80\ V,\ Hg^+/Hg = +0.79\ V,$$
$$Mg^{2+}/Mg = -2.37\ V,\ Cr^{3+}/Cr = -0.74\ V.$$

77. What is electrochemical series ? How does it help in calculating the e.m.f. of a standard cell ? *(Haryana Board 1995)*

Corrosion

78. What is corrosion ? Give the mechanism of rusting on the basis of electrochemical theory.
79. Suggest methods for the prevention of rusting.
80. What metal you might fasten to the hull of aluminium boat to give it cathodic protection ? Name two metals which cannot be used.
81. What is corrosion ? What are the factors which affect corrosion ?
82. CO_2 is always present in natural water. Explain its effects (increases, stops or no effect) on rusting of iron.
83. Rusting of iron is quicker in saline water than in ordinary water. Explain.
84. Explain
    (*i*) the function of a salt bridge in electrochemical cell.
    (*ii*) mechanism of rusting of iron. *(P.S.E.B. 1993)*
85. What is meant by the term cathodic protection of iron ?
86. Can we use aluminium or copper for cathodic protection of iron ? Explain giving reasons.
87. What is corrosion ? Give mechanism of rusting of iron. What do you understand by sacrificial protection of corrosion ? *(P.S.E.B. 1995)*

Electrolysis

88. What is electrolysis ? Describe the criteria for the formation of products at the respective electrodes.
89. Explain the following :
    (*i*) Concentrated aqueous HCl can be used to clear oxidised copper (copper containing a coating of copper (II) oxide) without attacking the copper metal.
    (*ii*) Sodium metal cannot be produced by the electrolysis of aqueous solution of sodium chloride.
90. During electrolysis of dilute aqueous solution of NaCl the oxidation of Cl^- ion occurs at the anode in preference to oxidation of H_2O. Explain why.
91. Using E° values explain the formation of products in electrolysis of :
    (*i*) aqueous $CuSO_4$ solution using platinum electrodes
    (*ii*) aqueous $CuSO_4$ solution using copper electrodes.
92. Predict the products of electrolysis of each of the following :
    (*i*) An aqueous solution of $AgNO_3$ with silver electrodes.
    (*ii*) An aqueous solution of $AgNO_3$ with inert electrodes.
    (*iii*) A dilute aqueous solution of H_2SO_4.
    (*iv*) An aqueous acidified solution of cupric chloride using platinum electrodes.

NUMERICAL PROBLEMS

93. Zinc rod weighing 25 g was kept in 100 ml of 1 M $CuSO_4$ solution. After a certain time interval the molarity of Cu^{2+} was found to be 0.8 M. What is molar concentration of SO_4^{2-} ions in solution ? What should be the mass of zinc rod after cleaning and drying ?

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94. Three electrolytic cells A, B and C containing electrolytes zinc sulphate, silver nitrate and copper sulphate respectively, were connected in series. A steady current of 1.50 ampere was passed through them until 1.50 g of silver were deposited at the cathode of cell B. How long did the current flow ? What masses of copper and of zinc were deposited ? (At. masses of Ag, Zn, Cu are 108, 65, 63.65 respectively).

95. A conductivity cell with electrodes 4 cm^2 in area and 1.5 cm apart has a resistance of 35.6 ohm when filled with 2.085% barium chloride solution. What is conductivity of $BaCl_2$ solution ?

96. A cell contains two hydrogen electrodes. The negative electrode is in contact with a solution of 10^{-6} M H^+ ions. If EMF of the cell is 0.118 at 25°C, calculate the conc. of H^+ ions at the positive electrode. Assume H_2 to be bubbled at 1 atm. pressure in each.

97. A measured voltage of the following cell is 0.900 V at 25°C. The cell is Pt, H_2 (1 atm.)/$H^+(aq)$ || Ag^+ (1.0 M)/Ag. If $E°_{Ag^+/Ag}$ = 0.80 V. Calculate the pH of the aqueous solution of H^+.

98. A current of 15 amp of used to plate nickel from $NiSO_4$ bath. Both H_2 and Ni are formed at cathode. The current efficiency with respect to formation of Ni is 60%.

(*a*) How many gram of nickel is plated per hour ?

(*b*) What volume of hydrogen is formed per hour ?

99. Four metals are labelled as A, B, C, D. They react with each other and with acids in the following way :

B displaces only C from solution.

A and D displace hydrogen from 1 M HCl.

None of the metals displace D from solution.

Arrange the metals in an activity series together with hydrogen.

100. How many coulombs of electricity are required to perform the following reductions. (Atomic mass of Sn = 118) :

(*i*) 1 g of Sn^{4+} to Sn^{2+} (*ii*) 250 ml of 0.1 M $Cu(NO_3)_2$ to Cu

(*iii*) 2×10^{-2} mol of Ca^{2+} to Ca (*iv*) 1 L of 0.05 M MnO_4^- to Mn^{2+}.

101. 5 L of 0.1 M $CuSO_4$ was to be electrolysed using a current strength of 2.0 amperes. But before electrolysis 10 g of zinc dust was added to the electrolytic cell. For how long the electrolysis has to be carried out in order to completely deposit copper from the solution. (Atomic masses of copper and zinc are 63.5 and 65 respectively.)

102. 40 ml of 0.126 M $NiSO_4$ solution is electrolysed by a current of 0.05 amp. for 40 minutes.

(*a*) Write equations for the reactions occurring at each electrode.

(*b*) How many coulombs of electricity are passed through the electrolyte ?

(*c*) How many grams of product is deposited at cathode ?

(*d*) How long the same current will have to be passed to remove completely the metal ions from the solution ?

103. The zinc/silver oxide cell, used in hearing aids and electrical watches involves following reactions.

$$Zn \longrightarrow Zn^{2+} + 2e^- ; \quad E° = 0.76 \text{ V}$$

$$Ag_2O + H_2O + 2e^- \longrightarrow 2Ag + 2OH^- ; \quad E° = 0.344 \text{ V}$$

(*a*) What is oxidised and what is reduced ?

(*b*) Find $E°_{cell}$ and $\Delta G°$.

104. Calculate the EMF of the cell

$$Mg(s)/Mg^{2+}(0.2 \text{ M}) \parallel Ag^+(1 \times 10^{-3} \text{ M})/Ag$$

$$E°_{Mg^{2+}/Mg} = -2.37 \text{ V}, E°_{Ag^+/Ag} = +0.80 \text{ V}$$

What will be the effect of EMF if concentration of Mg^{2+} ion is decreased to 0.1 M ?

105. Crude copper containing iron and silver as impurities was subjected to electro-refining by passing a current of 175 A for 386 seconds. The mass of anode was found to decrease by 22.260 g and that of cathode was increased by 22.011 g. Estimate the percentage of Cu, Fe and Ag in the crude sample.

$$E°_{Fe^{2+}/Fe} = -0.44 \text{ V and } E°_{Cu^{2+}/Cu} = +0.34 \text{ V}.$$

[**Hint.** Fe and Cu from anode will go into solution as Fe^{2+} and Cu^{+2} while Ag will settle as anode mud. Deposition at cathode will be solely Cu.]

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106. Given that $E^\circ_{Cu^{2+}/Cu^+} = 0.15$ V and $E^\circ_{Cu^{2+}/Cu} = 0.34$ V. Explain why copper (I) sulphate does not exist in aqueous solutions.

107. The resistance of 0.01 M NaCl solution in a conductivity cell was found to be 210 Ω. The equivalent conductance of this solution is 4.5×10^{-3} S cm^2 eq^{-1}. What is the cell constant of the cell ? *(CBSE 1992)*

108. What will be the reduction potential of the half cell $Fe^{3+}(0.01\ M)/Fe^{2+}(1\ M)$.

Given that $Fe^{2+} \longrightarrow Fe^{3+}$; $E^\circ = -0.77$.

109. For the galvanic cell :

$$Ag/AgCl(s), KCl\ (0.2\ M) \parallel KBr\ (0.001\ M), AgBr(s)/Ag$$

assign correct polarity to each electrode for a spontaneous process taking into account the cell reaction at 25°C

$K_{sp}(AgCl) = 2.8 \times 10^{-10}$; $K_{sp}(AgBr) = 3.3 \times 10^{-13}$ *(I.I.T. J.E.E. 1992)*

110. Calculate the standard electrode potential of Ni^{2+}/Ni electrode if the cell potential of a cell $Ni/Ni^{2+}\ (0.01\ M) \parallel Cu^{2+}\ (0.1\ M)/Cu$ is 0.59 V. Given that $E^\circ_{Cu^{2+}/Cu} = +0.34$ V. *(CBSE 1993)*

111. If a current of 0.200 A is passed through 50 ml of $\frac{M}{10}$ NaCl solution for 10 min. Calculate the concentration of OH^- ions in the solution after the electrolysis.

112. Calculate the maximum possible electrical work that can be obtained from the following cell under standard conditions at 25°C

$$Zn/Zn^{2+}(aq) \parallel Cu^{2+}(aq)/Cu$$

At 25°C, $E^\circ_{Zn^{2+}(aq)/Zn} = -0.76$ V, $E^\circ_{Cu^{2+}(aq)/Cu} = +0.34$ V,

$F = 96500$ C mol^{-1} *(CBSE 1995)*

113. The measured e.m.f. at 25°C for the cell reaction

$$Zn(s) + Cu^{2+}\ (1.0\ M) \longrightarrow Cu(s) + Zn^{2+}\ (0.1\ M) \text{ is 1.3 volt.}$$

Calculate E° for the cell reaction. *(P.S.E.B. 1995)*

114. The Edison storage cell is represented as

$$Fe(s)/FeO(s) \mid KOH(aq) \mid Ni_2O_3(s)/Ni(s)$$

The half-cell reactions are

$$Ni_2O_3(s) + H_2O(l) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-; \quad E^\circ = +0.40\ V$$

$$FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-; \quad E^\circ = -0.87\ V$$

(*i*) What is the cell reaction ?

(*ii*) What is the cell e.m.f. ? How does it depend on the concentration of KOH ?

(*iii*) What is the maximum amount of electrical energy that can be obtained from one mole of Ni_2O_3 ?

(I.I.T. 1994)

115. The standard reduction potential of the Ag^+/Ag electrode at 298 K is 0.799 V. Given that for AgI, $K_{sp} = 8.7 \times 10^{-17}$, evaluate the potential of the Ag^+/Ag electrode in a saturated solution of AgI. Also calculate the standard reduction potential of the $I^-/AgI/Ag$ electrode. *(I.I.T. 1994)*

116. An excess of liquid mercury is added to an acidified solution of 1.0×10^{-3} M Fe^{3+}. It is found that 5% of Fe^{3+} remains at equilibrium at 25°C. Calculate $E^\circ_{(Hg^{2+}/Hg)}$, assuming that the only reaction that occurs is

$$2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}.$$

(Given $E^\circ_{(Fe^{3+}/Fe^{2+})} = 0.77$ V). *(I.I.T. 1995)*

117. Calculate the standard potential of Fe^{3+}/Fe couple from the data given below. E° values for Fe^{2+}/Fe and Fe^{3+}/Fe^{2+} are respectively as −0.44 V and 0.77 V.

118. The standard reduction potential for Cu^{2+}/Cu is 0.34 V. Calculate the reduction potential at pH = 14 for the above couple. K_{sp} of $Cu(OH)_2$ is 1.0×10^{-19}. *(I.I.T. 1996)*

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119. How many grams of silver could be plated out on a serving tray by electrolysis of a solution containing silver in + 1 oxidation state for a period of 8.0 hrs at a current of 8.46 Amperes. What is the area of the tray if the thickness of silver plating is 0.00254 cm. Density of silver is 10.5 g cm^{-3}. *(I.I.T. 1997)*

120. Electrolysis of a solution of $MnSO_4$ in aqueous sulphuric acid is a method for the preparation of MnO_2 as per the chemical reaction

$$Mn^{2+}(aq) + 2H_2O \longrightarrow MnO_2(s) + 2H^+ + H_2(g)$$

Passing a current of 27 Amp. for 24 hrs gives one kg of MnO_2. What is the current efficiency and what are the reactions occuring at cathode and anode ? *(I.I.T. 1997)*

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FOR THE COMPETITIVE EXAMS

MULTIPLE CHOICE QUESTIONS

- ***Select the correct answer from questions (1—43) :***

1. If the cell reaction is spontaneous
   (*a*) E° is – ve (*b*) ΔG is + ve (*c*) e.m.f. is + ve (*d*) (G + E°) is + ve.
2. The cell reaction $Zn + Cu^{2+} \longrightarrow Zn^{2+} + Cu$ is best represented by
   (*a*) $Cu \mid Cu^{2+} \parallel Zn^{2+} \mid Zn$ (*b*) $Pt \mid Zn^{2+} \parallel Cu^{2+} \mid Pt$
   (*c*) $Zn \mid Zn^{2+} \parallel Cu^{2+} \mid Cu$ (*d*) any of the above.
3. In an electrochemical cell
   (*a*) Potential energy changes into kinetic energy (*b*) Potential energy changes into chemical energy
   (*c*) Kinetic energy changes into potential energy (*d*) Chemical energy changes into electrical energy.
4. Which one of the following does not hold good for normal hydrogen electrode ?
   (*a*) The hydrogen gas pressure is two atmospheres (*b*) The concentration of H^+ ions in its solution is 1 M
   (*c*) The temperature is 298 K
   (*d*) The electrode of Pt, coated with platinum black is used.
5. The cell potential, E_{cell} is equal to
   (*a*) $E_{cathode} + E_{anode}$ (*b*) $E_{anode} - E_{cathode}$ (*c*) $E_{cathode} - E_{anode}$ (*d*) $E_{left} - E_{right}$.
6. The function of the salt bridge is to
   (*a*) allow ions to move from anode to cathode
   (*b*) allow solutions from one-half cell to the other half-cell
   (*c*) allow the current to flow through the cell and keep the solutions electrically neutral
   (*d*) keep the level of solutions same.
7. Which one of following is an incorrect statement for an electro-chemical cell ?
   (*a*) The oxidizing and reducting agents should be separated from each other
   (*b*) A salt bridge containing the same electrolyte solution as present in oxidation half cell should be used to internally connect the two half cells
   (*c*) The cell stops working after some time
   (*d*) The circuit is completed externally by connecting a wire to the electrodes.
8. Which one of the following is incorrect in a galvanic cell ?
   (*a*) The electrode at which oxidation takes place is called an anode
   (*b*) The electrode at which electrons are gained is called cathode
   (*c*) The electrode at which reduction takes place is called cathode
   (*d*) The electrode at which electrons are lost is called cathode.
9. The units of equivalent conductivity of solution are :
   (*a*) Ω^{-1} (*b*) Ω^{-1} cm equiv.$^{-1}$ (*c*) Ω^{-1} cm equiv. (*d*) Ω^{-1} cm^2 equiv^{-1}.
   (Pb. CET 1991)
10. According to Kohlrausch's law the value of Λ_m^∞ of an electrolyte x_2y which dissociates as $2x^+ + y^-$ is given by
   (*a*) $\lambda_{x^+}^\infty + \lambda_{y}^\infty$ (*b*) $\lambda_{x^+}^\infty - \lambda_{y^-}^\infty$ (*c*) $\lambda_{x^+}^\infty + \lambda_{y^-}^\infty$ (*d*) none of the above.

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11. If x is the specific resistance of the electrolyte solution and y is the molarity of the solution, then Λ_m is given by
(a) $\frac{1000\,y}{x}$ (b) $\frac{1000\,x}{y}$ (c) $\frac{xy}{1000}$ (d) $\frac{1000}{xy}$.

12. The equation giving the relationship between E, E° and concentration of ions in a half cell, is called
(a) Kohlrausch's equation (b) Nernst equation (c) Ohm's equation (d) Pauling's equation.

13. Which of the following solutions will turn blue on adding piece of copper metal to it
(a) $KNO_3(aq)$ (b) $MgCl_2(aq)$ (c) $ZnSO_4(aq)$ (d) $AgNO_3(aq)$.

14. How long 2 amp. current should be passed to supply 72000 C of charge ?
(a) 1 hr (b) 10 hr (c) 15 hr (d) none of the above.

15. Which of the following cells can convert chemical energy of H_2 and O_2 directly into electrical energy ?
(a) Mercury cell (b) Daniell cell (c) Lead storage cell (d) Fuel cell.

16. Zinc is used to protect iron from corrosion because
(a) E_{oxi} of zinc is less than E_{oxi} of iron (b) E_{red} of zinc is less than E_{red} of iron
(c) zinc is cheaper than iron (d) zinc is abundantly available.

17. The charge required for the reduction of 1 mol. of $Cr_2O_7^{2-}$ ions to Cr^{3+} is
(a) 96500 C (b) 2 × 96500 C (c) 6 × 96500 C (d) 4 × 96500 C.

18. The approximate voltage of dry cell is
(a) 2.0 V (b) 1.2 V (c) 1.5 V (d) 6 V.

19. In which of the cells does the following reaction occur,

$$\frac{1}{2}H_2(g) + AgCl(s) \longrightarrow H^+(aq) + Ag(s)$$

(a) $Ag/AgCl(s)$; $KCl(aq) \parallel AgNO_3(aq)/Ag$ (b) $Pt, H_2(g)/HCl(aq) \parallel AgNO_3(aq)/Ag$
(c) $Pt, H_2(g)/HCl(aq) \parallel AgCl(s)—KCl(aq)/Ag$ (d) $Pt, H_2(g)/KCl(aq) \parallel AgCl(s)—KCl(aq)/Ag$.
(I.I.T. 1985)

20. Other things beings equal, the life of a Daniell cell may be increased by
(a) Keeping low temperature (b) Using large copper electrodes
(c) Decreasing concentration of copper ions (d) Using large zinc electrodes. *(Pb. CET 1988)*

21. The ionic conductivity of the cation and anion of the uni-univalent salt is 140 and 80 respectively. The molar conductivity of the salt is
(a) $160\ \Omega^{-1}\ cm^2\ mol^{-1}$ (b) $280\ \Omega^{-1}\ cm^2\ mol^{-1}$ (c) 60 moles (d) $220\ \Omega^{-1}\ cm^2\ mol^{-1}$.
(CEET 1991)

22. When lead storage bettery discharges
(a) SO_2 is evolved (b) $PbSO_4$ is consumed
(c) Lead is formed (d) Sulphuric acid is consumed. *(Pb. CET 1991)*

23. The amount of electricity required to deposit 1 mole of aluminium from a solution of $AlCl_3$ will be
(a) 0.33 Faraday (b) 1 Faraday (c) 3 Faraday (d) 1.33 Faraday.

24. The element with highest electrical conductivity is
(a) Gold (b) Silver (c) Copper (d) Mercury.

25. The mass of a substance liberated at an electrode is directly proportional to
(a) Atomic mass (b) Equivalent mass
(c) Molecular mass (d) Formula mass of the ion.

26. The resistance of a metallic conductor
(a) Decreases with temperature (b) Is independent of temperature
(c) Increases with temperature (d) May increase or decrease with temperature.

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27. The chemical reaction taking place at the anode is
(*a*) Oxidation (*b*) Dissociation (*c*) Reduction (*d*) Deposition.

28. Passage of electricity through dilute H_2SO_4 for 1 hour liberates a total of 224 ml of H_2 at N.T.P. The strength of current would be
(*a*) 0.27 amperes (*b*) 0.54 amperes (*c*) 0.042 amperes (*d*) 0.027 amperes.

29. Molten NaCl conducts electricity due to presence of
(*a*) Free electrons (*b*) Free molecules (*c*) Free ions (*d*) Atoms of Na and Cl.

30. Faraday's laws of electrolysis are related to
(*a*) Atomic number of the cation (*b*) Atomic number of the anion
(*c*) Equivalent mass of the electrolyte (*d*) Speed of the cation.

31. How many electrons are delivered to the cathode during electrolysis by a current of 1 ampere in 60 seconds ?
(*a*) 6.0×10^{23} (*b*) 6.0×10^{20} (*c*) 3.74×10^{20} (*d*) 7.48×10^{21}.

32. The electrode Pt, $H_2(g)$/HCl is reversible with respect to
(*a*) Cl^- ions (*b*) HCl (*c*) H^+ ions (*d*) Both H^+ and Cl^- ions.

33. Which one of the following dissolved in water forms a solution that is non-conducting ?
(*a*) Chile saltpetre (*b*) Potash alum (*c*) Green vitriol (*d*) Ethyl alcohol.

34. For the electrolysis of dil H_2SO_4 using platinum electrodes which of the following statements is correct ?
(*a*) Hydroxide ions are discharged at cathode (*b*) Hydrogen is evolved at anode
(*c*) Oxygen is the only gas evolved (*d*) A chemical change occurs.

35. Two platinum electrodes are immersed in a $CuSO_4$ solution and a current is passed. Slowly the colour of the $CuSO_4$ disappears and glass appear at the electrodes ; leaving behind a colourless solution. The colourless solution is
(*a*) Water (*b*) Platinum sulphate solution
(*c*) Copper hydroxide (*d*) Sulphuric acid solution.

36. An aqueous solution of sulphuric acid is electrolysed using platinum electrodes. 0.48 g of oxygen is liberated at the anode and in the same time, the volume of gas liberated at the cathode (assuming one mole of gas at room temperature and pressure occupies 24 dm^3 and both gases are insoluble in dil H_2SO_4) is
(*a*) 0.48 dm^3 (*b*) 12.00 dm^3 (*c*) 0.72 dm^3 (*d*) 1.20 dm^3.

37. The equivalent conductance of an electrolyte increases as
(*a*) Dilution increases (*b*) Temperature decreases
(*c*) Dilution decreases (*d*) None of the above is correct.

38. When aqueous solution of NaCl is electrolysed the product obtained at the cathode is
(*a*) Hydrogen (*b*) Sodium metal (*c*) Oxygen (*d*) Chlorine.

39. When aqueous solution of NaCl is electrolysed at the end the solution left in the electrolytic cell is rich in
(*a*) NaCl (*b*) HCl (*c*) NaOH (*d*) is only water.

40. A dilute aqueous solution of Na_2SO_4 is electrolysed using platinum electrodes. The products at the anode and cathode are
(*a*) O_2, H_2 (*b*) $S_2O_8^{2-}$, Na (*c*) O_2, Na_6 (*d*) $S_2O_8^{2-}$, H_2.

(I.I.T. 1996)

41. The standard electrode potential (E°) for OCl^-/Cl^- and $Cl^-/\frac{1}{2}Cl_2$ respective respectly are 0.94 V and – 1.36 V. The E° value of $OCl^-/\frac{1}{2}Cl_2$ will be
(*a*) – 0.42 V (*b*) – 2.20 V (*c*) 0.52 V (*d*) 1.04 V.

(Kurukshetra CEET 1996)

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42. E°_{cell} of $Zn/Zn^{2+} \| Cu^{2+}/Cu$ is 1.10 V at 25°C, the equilibrium constant for the reaction $Zn + Cu^{2+} \rightleftharpoons Cu + Zn^{2+}$ is approximately of the order of

(*a*) 10^{-28} (*b*) 10^{+37} (*c*) 10^{-18} (*d*) 10^{17}.

(CBSE Med. 1997)

43. The standard reduction potential of Cu^{2+}/Cu and Cu^{2+}/Cu^{+} are 0.337 and 0.153 V respectively. The standard electrode potential of Cu^{+}/Cu half cell will be

(*a*) 0.184 V (*b*) 0.827 V (*c*) 0.521 V (*d*) 0.490 V. ***(I.I.T. 1997)***

ASSERTION-REASON TYPE QUESTIONS

In each of the following questions, two statements are given. One is labeled as *Assertion 'A'* and the other one as *Reason R*. Examine both the statements and mark the correct choice *a*, *b*, *c* or *d* according to the following instructions.

(*a*) If both **A** and **R** are correct and **R** is correct explanation of **A**

(*b*) If both **A** and **R** are correct but **R** is not the explanation of **A**

(*c*) If **A** is correct **R** is wrong

(*d*) If **A** is wrong **R** is correct.

44. ***Assertion* A** : The reduction potential of the electrode can be increased by increasing the concentration of metal cations.

***Reason* R** : E is directly proportional to $[M^{n+}]$.

(*a*) (*b*) (*c*) (*d*)

45. ***Assertion* A** : Zn and iron cannot decompose water to librate hydrogen gas.

***Reason* R** : $E^\circ_{Zn/Zn^{2+}}$ and $E^\circ_{Fe/Fe^{2+}}$ are lower than $E^\circ_{H_2/H^+}$.

(*a*) (*b*) (*c*) (*d*)

46. ***Assertion* A** : Zinc protects the iron better than tin even after the cracks.

***Reason* R** : Oxidation potential of Zn > Fe but oxidation potential of Sn < Fe.

(*a*) (*b*) (*c*) (*d*)

47. ***Assertion* A** : The voltage of isolated half cell is not possible to be measured.

***Reason* R** : Oxidation or reduction cannot take place alone.

(*a*) (*b*) (*c*) (*d*)

48. ***Assertion* A** : Electrolytic conduction increases with increase in temperature.

***Reason* R** : Increase in temperature cause the electronic movement more rapid.

(*a*) (*b*) (*c*) (*d*)

FILL IN THE BLANKS

1. The electrode at which there is acceptance of electrons is called ..... .
2. The conductance of a solution placed between two opposite faces of a centimetre cube is called ..... .
3. The solution of sugar in water is ..... conductor of electricity.
4. Strong electrolytes give almost linear plot of Λ_m versus ..... .
5. The resistance of a solution is measured with the help of .....
6. An aqueous solution of copper nitrate ..... be stored in an iron vessel.

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7. In a Daniell cell, the copper vessel serves as ..... .
8. The E° value of normal hydrogen electrode is ..... .
9. A galvanic cell stops after some time because ..... .
10. In a galvanic cell, the electrons flow from ..... to ..... through connecting wires.
11. The unit of specific resistance is ..... .
12. The equivalent conductance of a solution ..... with decrease in concentration of the electrolyte in the solution.
13. When aqueous solution of copper sulphate is electrolysed using platinum electrodes, the gas liberated at cathode is ..... .
14. A device in which chemical energy of a fuel is directly converted into electrical energy is called ..... .
15. The chemical formula of rust is ..... .
16. In galvanized iron, the iron is coated with a layer of ..... metal.
17. The main function of salt bridge in an electrochemical cell is to ..... .
18. The molar conductance (Λ_m) of a solution is related to specific conductance (k) by the relation ..... .
19. In representation of an electrochemical cell, the cathode is written on ..... .
20. Specific conductance of an electrolytic solution ..... with increase in dilution.
21. A solution of sodium in liquid ammonia conducts electricity at – 33°C. On further cooling the conductivity of the solution ..... . *(I.I.T. 1997)*

TRUE/FALSE STATEMENTS

1. The unit of specific conductance is ohm cm^{-1}.
2. The numerical value of equivalent conductance may be equal to or less than the molar conductance.
3. The value of Λ_m for strong electrolytes is less than the value for weak electrolytes.
4. The molar conductivity at infinite dilution for strong electrolytes can be obtained by extrapolating the graph of Λ_m *vs* $\sqrt{C}$.
5. In an electrochemical cell the anode constitutes the negative terminal.
6. In an electrochemical cell, the electrode having higher reduction potential acts as anode.
7. As the electrochemical cell functions, the electrode potential of anode decreases while that of cathode increases.
8. The electrochemical cell stops working after some time because EMF of the cell becomes zero.
9. The equilibrium constant for a cell reaction is directly proportional to the standard EMF of the cell.
10. In aqueous solution of copper sulphate the products of electrolysis, using platinum electrodes, are copper and oxygen.
11. Molar conductivity of solution changes with dilution.
12. Λ_m of solution increases with dilution.
13. The anode is an electrode connected to – ve terminal of battery in electrolysis.
14. Direct current is used for measuring the resistance of electrolyte by wheatstone bridge.
15. Salt bridge helps to maintain the electrical neutrality of the solution in two half cells.
16. According to the electrochemical series, potassium is more reactive as compared to zinc.
17. Electrochemical series helps to predict the feasibility of a reaction.
18. In dry cell, zinc vessel itself acts as cathode.
19. The amount of a substance liberated at an electrode, during electrolysis, is directly proportional to its molecular mass or atomic mass.

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MATCHING TYPE QUESTIONS

Match the items of column A and B :

Column A	Column B
1. Molar conductivity	1. Siemens cm^{-1}
2. Dry cell	2. Nernst Equation
3. Zn/Zn^{2+} (0.1 M) ‖ Zn^{2+} (0.5 M)/Zn	3. Maximum work obtainable from cell
4. Specific conductivity	4. Primary cell
5. $E = E^\circ + \frac{0.059}{n} \log \frac{[M^{n+}]}{[M]}$	5. $Ohm^{-1}\ cm^2\ mol^{-1}$
6. E°_{cell}	6. concentration cell
7. 96500 C mol^{-1}	7. Siemen's cm^2
	8. Faraday's constant

ANSWERS/HINTS

REVIEW PROBLEMS

5.1. A **5.2.** 2.06×10^{-3} S cm^{-1} **5.3.** 21.5 $\Omega^{-1}\ cm^2$ equ.$^{-1}$

5.4. 1240 S $cm^2\ mol^{-1}$ **5.5.** 235.5 S $cm^2\ mol^{-1}$

5.6. 40 $\Omega^{-1}\ cm^2\ mol^{-1}$ [**Hint** : Cell constant = 2/4 = 0.5 cm^{-1}]

5.7. (*i*) $6.25 \times 10^5\ \Omega$ (*ii*) 1.6×10^{-6} amp. **5.8.** 0.129 $\Omega^{-1}\ cm^{-1}$

5.9. (*i*) $1 \times 10^{-2}\ \Omega^{-1}$ (*ii*) $1 \times 10^{-2}\ \Omega^{-1}\ cm^{-1}$ (*iii*) $10^2\ \Omega$ cm

5.10. 73.5 $ohm^{-1}\ cm^2\ mol^{-1}$ **5.11.** 138.4 S $cm^2\ mol^{-1}$ **5.12.** 1.3%, 4.1%, 12.5%

5.13. 393 $\Omega^{-1}\ cm^2\ mol^{-1}$ **5.14.** – 0.79 V **5.15.** 2

5.16. 1.59×10^{-9} M **5.17.** 0.2804 V **5.18.** 0.6093 V

5.19. 1.635 V **5.20.** 0.0403 **5.21.** 8.5×10^{15}

5.22. 1×10^{90} **5.23.** 8.556×10^{27} **5.24.** 2.6×10^{25}

5.25. – 84.92 J **5.26.** – 474.4 kJ **5.27.** -2.123×10^5 J

5.28. 0.333 g of Cl_2 **5.29.** 1.99 hrs **5.30.** 1.78 g

5.31. (*i*) 96500 C (*ii*) 536111.1 C **5.32.** 2.73 g

VERY SHORT ANSWER QUESTIONS

1. Oxidation no. of N changes from + 3 to – 3. Hence 6 mol of electrons are required.
2. 130 $Ohm^{-1}\ cm^2\ equ^{-1}$
3. Yes
4. Hydrogen gas
5. $Fe_2O_3.xH_2O$
6. Aqueous KOH or Aqueous NaOH ; $\eta = \frac{\Delta G}{\Delta H} = \frac{-nFE}{\Delta H}$
7. 95%
8. Pt, H_2 (1 atm)/H^+(1 M) ‖ Cu^{2+} (1 M)/Cu
9. 96500, 6.02×10^{23}.

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10. No. Since $E^\circ_{Ag^+/Ag}$ is greater than that of copper. Hence Ag^+ ion will be reduced by copper atom according to the reaction $2\,Ag^+ + Cu \longrightarrow 2\,Ag + Cu^{2+}$

11. The products obtained are different (Refer section 5.20).

12. No. As it introduces resistance and changes the potential difference between two terminals.

15. + ve. **14. Anode :** $C_3H_8 + 6H_2O \longrightarrow 20e^- + 3CO_2 + 20H^+$

Cathode : $O_2 + 4H^+ + 4e^- \longrightarrow 2H_2O$

15. In a cell the partition is needed to separate the oxidising agent and reducing agent. In lead storage cell, the oxidant, PbO_2; reductant, Pb and their oxidation and reduction product $PbSO_4$, are all solids. Thus, half cells need not be in separate vessels and as such no partition is needed to separate them.

16. Electrical conductance increases with increase in temperature.

27. Molar conductivity of a weak electrolyte increases with decrease in concentration.

28. By increasing the concentration of ions in contact with electrode.

29. Zero. **32.** $2H_2O \longrightarrow O_2 + 4H^+ + 4e^-$. **38.** 96500 coulombs.

39. Molar conductivity increases with increase in temperature.

40. Because zinc vessel, which acts as anode, dissolves by reacting with the electrolyte which is acidic in nature.

DESCRIPTIVE QUESTIONS

62. (*a*) Au^{3+} (*b*) $AuCl_3(aq)$ (*c*) Cathode

63. (*a*) Decrease (*b*) Increase (*c*) Increase (*d*) no effect.

73. In the net cell reaction no ions are involved, consequently no change in ionic concentration. Hence, no variation in voltage.

75. Mg, Al, Zn, Fe, Cu.

90. Because Cl^- has lower reduction potential (higher oxidation potential) than H_2O.

NUMERICAL PROBLEMS

93. $[SO_4^{2-}] = 1$ M, 23.7 g **94.** 14.89 min ; 0.44 g of Cu ; 0.45 g of Zn

95. 0.011 S cm^2 mol^{-1} **96.** 10^{-4} M **97.** 1.69

98. 9.86 g, 2.51 L at STP **99.** Starting with least active metal : C, B, H, A, D

100. (*i*) 1635.58 C (*ii*) 4825 C (*iii*) 3860 C (*iv*) 24125 C

101. **Hint.** Zinc will displace copper ions. 10 g of zinc will displace 9.77 g of Cu from the solution.

$\therefore$ Cu^{2+} ions left in the solution = (31.75 – 9.77) g = 21.98 g **[Ans.** 9.27 hrs.]

102. (*b*) 120 C (*c*) 0.036 g (*d*) 5 hr. 21 min. 40 sec.

103. $E^\circ_{cell} = 1.104$ V, $\Delta G^\circ = -2.13 \times 10^5$ J **104.** 3.013 V, E_{cell} will increase to 3.02 V

105. Cu = 98.88%, Fe = 0.90%, Ag = 0.22%

106. **Hint.** Cu(I) undergoes disproportionation. Calculate e.m.f. of $2Cu^+ \longrightarrow Cu + Cu^{2+}$ which will come out to be positive indicating the feasibility of process.

107. 9.45×10^{-6} cm^{-1} **108.** 0.652 V

109. **Hint.** (*i*) Calculate solubilities of AgCl in 0.2 KCl and AgBr in 0.001 KBr solution.
(*ii*) Find reduction potential for each electrode.

110. $E^\circ_{Ni^2/Ni} = 0.22$ V **111.** 0.0248 M **112.** 212.3 kJ

113. $E = E^\circ + \frac{.059}{n} \log \frac{[Cu^{2+}][Zn]}{[Cu][Zn^{2+}]} = 1.3 + \frac{.059}{2} \log \frac{(1.0)(1)}{(1)(0.10)} = 1.3 + \frac{.059}{2} = 1.33$ V.

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114. (*i*) $Ni_2O_3(s) + H_2O(l) + 2e^- \rightleftharpoons 2NiO(s) + 2OH^-$; $E° = +0.40$ V

(*ii*) $FeO(s) + H_2O(l) + 2e^- \rightleftharpoons Fe(s) + 2OH^-$; $E° = -0.87$ V

The first electrode having higher reduction potential would act as cathode

Subtracting equation (*ii*) from (*i*), we get the **cell reaction :**

$$Ni_2O_3(s) + Fe(s) \longrightarrow 2NiO(s) + FeO(s)$$

$$EMF = E_{cathode} - E_{anode}$$

$$= 0.40 - (-0.87) = \mathbf{1.27\ V}$$

Maximum electrical work $= nFE°_{cell}$

$$= 2 \times 96500 \times 1.27 = 2.45 \times 10^5\ J = \mathbf{245\ kJ.}$$

115. $Ag^+ + e^- \longrightarrow Ag$ $\quad E°_{Ag^+/Ag} = 0.799$ V

In saturated solution of AgI, the following equilibrium exists.

$$AgI(s) \rightleftharpoons Ag^+(aq) + I^-(aq)$$

$$K_{sp} = [Ag^+][I^-]$$

$$K_{sp} = [Ag^+]^2 \qquad (\because [Ag^+] = [I^-])$$

$$[Ag^+] = \sqrt{K_{sp}} = \sqrt{8.7 \times 10^{-17}} = 9.3 \times 10^{-9}\ M$$

According to Nernst equation

$$E_{Ag^+/Ag} = E°_{Ag^+/Ag} + \frac{.059}{n} \log \frac{[Ag^+]}{[Ag]}$$

$$= 0.799 + \frac{.059}{1} \log (9.3 \times 10^{-9}) = \mathbf{0.325\ V.}$$

In order to calculate standard reduction potential of $I^-/AgI/Ag$ electrode first calculate solubility of AgI in 1 M I^- and then apply Nernst equation.

116. The reaction is : $2Hg + 2Fe^{3+} \longrightarrow Hg_2^{2+} + 2Fe^{2+}$

original $[Fe^{3+}] = 1 \times 10^{-3}$ M

$[Fe^{3+}]$ which remain of equilibrium $= \dfrac{5 \times 10^{-3}}{100} = 5 \times 10^{-5}$ M

Fe^{3+} ions converted into Fe^{2+} ions $= 1 \times 10^{-3} - 5 \times 10^{-5} = 9.5 \times 10^{-4}$ M

Hg_2^{2+} ions at equilibrium $= \dfrac{9.5 \times 10^{-4}}{2} = 4.75 \times 10^{-4}$ M

Apply Nernst equation $\quad E_{cell} = E°_{cell} + \dfrac{0.059}{2} \log \dfrac{[Fe^{3+}]^2}{[Hg_2^{2+}]\,[Fe^{2+}]^2}$

or $\quad 0 = E°_{cell} + \dfrac{0.059}{2} \log \dfrac{(5 \times 10^{-5})^2}{(4.75 \times 10^{-4})(9.5 \times 10^{-4})^2}$

or $\quad E°_{cell} = -0.0226$ V

Now, $\quad E°_{cell} = E°_{Fe^{3+}/Fe^{2+}} - E°_{Hg_2^{2+}/Hg}$

$\therefore \quad E°_{Hg_2^{2+}/Hg} = E°_{Fe^{3+}/Fe^{2+}} - E°_{cell}$

or $\quad = 0.77 - (-0.0226) = \mathbf{0.7976\ V}$

117. Proceed according to solved *example 5.28.*

$$E°_{Fe^{3+}/Fe} = -0.04\ V$$

118. In a solution with pH = 14 $\therefore$ $[H^+] = 1 \times 10^{-14}$ $\therefore$ $[OH^-] = 10° = 1$ M

$$Cu(OH)_2 \rightleftharpoons Cu^{2+} + 2OH^-$$

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$$K_{sp} = [Cu^{2+}][OH^-]^2 \quad \text{or} \quad 1.0 \times 10^{-19} = [Cu^{2+}](1)^2 \quad \text{or} \quad [Cu^{+2}] = 10^{-19}\ M$$

$$Cu^{2+} + 2e^- \longrightarrow Cu$$

According to Nernst equation, $E = E^\circ + \frac{0.059}{2} \log [Cu^{2+}]/[Cu]$

$$= 0.34 + 0.029 \log (10^{-19}) \quad \text{or} \quad E = -0.22\ V.$$

119. $Ag^+ + e^- \longrightarrow Ag$

Quantity of electricity passed $= 8 \times 60 \times 60 \times 8.40\ C = 243648\ C$

Silver deposited by 243648 C of electricity $= \frac{108 \times 243648}{96500} = 272.68\ g$

Volume of Ag deposited $= \frac{272.68\ (g)}{10.5\ g\ cm^{-3}} = 25.96\ cm^3$

or Area of tray $= \frac{\text{Volume}}{\text{Thickness}} = \frac{25.96}{0.00254} = 10220.4\ cm^3$

120. $Mn^{2+} \longrightarrow \overset{+4}{MnO_2} + 2e^-$

Quantity of electricity passed $= 27 \times 24 \times 60 \times 60\ C = 2332800\ C$

Amount of MnO_2 produced theoretically $= \frac{87 \times 2332800}{2 \times 96500} = 1051.57\ g$

Amount of MnO_2 actually produced $= 1\ kg = 1000\ g$

Current efficiency $= \frac{1000}{1051.57} = 0.950 = 95\%$

Cathodic reaction : $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

Anodic reaction : $Mn^{2+} + 2OH^- \longrightarrow MnO_2 + 2H^+ + 2e^-$.

MULTIPLE CHOICE QUESTIONS

1. (*c*)	**2.** (*c*)	**3.** (*d*)	**4.** (*a*)	**5.** (*c*)	**6.** (*c*)
7. (*b*)	**8.** (*d*)	**9.** (*d*)	**10.** (*d*)	**11.** (*d*)	**12.** (*b*)
13. (*d*)	**14.** (*b*)	**15.** (*d*)	**16.** (*b*)	**17.** (*c*)	**18.** (*c*)
19. (*c*)	**20.** (*a*)	**21.** (*d*)	**22.** (*d*)	**23.** (*c*)	**24.** (*b*)
25. (*b*)	**26.** (*c*)	**27.** (*a*)	**28.** (*b*)	**29.** (*c*)	**30.** (*c*)
31. (*c*)	**32.** (*c*)	**33.** (*d*)	**34.** (*d*)	**35.** (*d*)	**36.** (*c*)
37. (*a*)	**38.** (*a*)	**39.** (*c*)	**40.** (*a*)	**41.** (*a*)	**42.** (*b*)
43. (*c*)	**44.** (*a*)	**45.** (*d*)	**46.** (*a*)	**47.** (*a*)	**48.** (*c*).

FILL IN THE BLANKS

1. Cathode	**2.** Specific conductance	**3.** bad
4. $\sqrt{C}$	**5.** Wheatstone bridge	**6.** can
7. Cathode	**8.** Zero	**9.** Potential difference becomes zero
10. anode, cathode	**11.** ohm-cm	**12.** increases
13. Hydrogen	**14.** Fuel cells	**15.** $Fe_2O_3 . xH_2O$
16. Zinc	**17.** Electrical neutrality	**18.** $\Lambda_m = \frac{k \times 10^3}{M}$
19. Left hand side	**20.** Decreases.	

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TRUE FALSE STATEMENTS

1. False	2. True	3. False	4. False	5. True	6. False
7. False	8. True	9. True	10. True	11. True	12. True
13. False	14. False	15. True	16. True	17. True	18. False
19. False.					

MATCHING TYPE QUESTIONS

1—5 2—4 3—6 4—1 5—2 6—3 7—8.

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6

Chemical Kinetics

LEARNING OBJECTIVES

In this Unit, we shall learn

- *Rate expression ;*
- *Order of reaction (with suitable examples) ;*
- *Units of rate and specific rate constant ;*
- *Order of reaction and concentration (study confined to 1st order) ;*
- *Temperature dependance of rate constant ;*
- *Fast reactions (elementry idea) ;*
- *Photochemical reactions ;*
- *Mechanism of reactions (elementry idea).*

During the course of our studies we come across a wide variety of chemical reactions having different rates. In thermodynamics (unit 4) we have studied that the decrease in free energy ($\Delta G < 0$) is quite helpful in predicting the feasibility of chemical reactions. However, knowledge of free energy change of reaction does not give any idea about the speed or rate of the reaction.

In general, various reactions can be categorised into three types depending upon the reaction rates.

1. *Very fast reactions.* This type consists of reactions which occur almost instantaneously. For example, the precipitation of AgCl occurs instantaneously by addition of aqueous solution of sodium chloride to aqueous solution of silver nitrate.

$$AgNO_3(aq) + NaCl(aq) \longrightarrow AgCl(s) + NaNO_3(aq)$$

The rates of such reactions (ionic reactions) cannot be determined easily.

The obvious reason for a very fast rate of such reactions is that no chemical bonds are to be broken among the reactants.

2. *Very slow reactions.* This type comprises reactions which occur at a very slow rate. These reactions may require months or even years together for their completion. For example, rusting of iron.

The rates of such reactions are hardly of any physical importance.

3. *Moderately slow reactions.* This type refers to reactions in between the very fast (*type 1*) and very slow (*type 2*) reactions. These reactions proceed at moderate speed which can be easily measured. Inversion of cane sugar and hydrolysis of starch are common examples of this type of reactions.

$$\underset{\text{Cane sugar}}{C_{12}H_{22}O_{11}} + H_2O \longrightarrow \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$2(C_6H_{10}O_5)_n + nH_2O \longrightarrow \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

Such type of chemical reactions will be the main focus of our study in this chapter. ***The branch of chemistry which deals with the study of reaction rates and their mechanisms is called*** **Chemical Kinetics.**

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The kinetic studies not only help us to determine the reaction rates but also describe the conditions by which the reaction rates can be altered. Besides this the mechanism governing the reactions could also be predicted on the basis of logical kinetic data.

6.1. RATE OF A CHEMICAL REACTION

The rate of a chemical reaction can be expressed *qualitatively* as well as *quantitatively*. The qualitative rate is not of any significance because it merely provides us with arbitrary conclusions about the rate of a reaction. These conclusions are based on certain visual parameters like disappearance of reactants, colour change, effervescence, etc. On the other hand, the quantitative rate of a chemical reaction provides us with much better information about the rate data and the accurate rate of a reaction.

Quantitatively, the *rate of chemical reaction* may be defined as *the speed or velocity at which the reactants change into products.* The rate of a reaction may be expressed in any of the following ways :

(*i*) *The rate of decrease in concentration of any one of the reactant,* or

(*ii*) *The rate of increase in concentration of any one of the product.*

For example, for a hypothetical reaction

$$A \longrightarrow B$$

$$\text{Rate of disappearance of A} = \frac{\text{Decrease in conc. of A}}{\text{Time taken}} = -\frac{\Delta[A]}{\Delta t}.$$

Or

$$\text{Rate of appearance of B} = \frac{\text{Increase in conc. of B}}{\text{Time taken}} = +\frac{\Delta[B]}{\Delta t}$$

While writing the expressions for rate we use a negative sign in the expression employed for expressing rate in terms of reactants.

Significance of Negative Sign

The negative sign in first expression does not mean that the rate is negative, rather it indicates the decrease in concentration of the reactant. As we know that with passage of time the concentrations of reactants decrease, therefore, the change in concentration, Δ[A] (Final conc.—Initial conc.) will have a negative value. Since the rate of a reaction is a positive quantity, thus, to get a positive rate we put a – ve sign in the rate expression.

Thus, *Rate of reaction = Rate of disappearance of A = Rate of appearance of B*

$$= -\frac{\Delta[A]}{\Delta t} \qquad = \frac{\Delta[B]}{\Delta t}$$

The square brackets around the formulae of various substances are used to express the concentration in $mol\ L^{-1}$. Thus, [A] stands for concentration of substance A in $mol\ L^{-1}$.

Now let us further elaborate the same idea for writing mathematical expression for the rates of chemical reactions by taking different examples.

1. Reactions involving same stoichiometric coefficients of all the reactants and products.

Let us consider the gaseous reaction between nitrogen dioxide and carbon monoxide.

$$NO_2(g) + CO(g) \longrightarrow CO_2(g) + NO(g)$$

In this case, as the reactants and products appear in ***same stoichiometric proportions,*** therefore, the rate of the reaction may be expressed in terms of rate of disappearance of nitrogen dioxide or carbon monoxide or alternatively, by the rate of appearance of carbon dioxide or nitric oxide whichever may be convenient.

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Thus, rate of reaction is given by

$$\textit{Rate of reaction} = \begin{bmatrix}\text{rate of}\\ \text{disappearance}\\ \text{of } NO_2\end{bmatrix} = \begin{bmatrix}\text{rate of}\\ \text{disappearance}\\ \text{of CO}\end{bmatrix} = \begin{bmatrix}\text{rate of}\\ \text{appearance}\\ \text{of } CO_2\end{bmatrix} = \begin{bmatrix}\text{rate of}\\ \text{appearance}\\ \text{of NO}\end{bmatrix}$$

$$= -\frac{\Delta[NO_2]}{\Delta t} \qquad = -\frac{\Delta[CO]}{\Delta t} \qquad = \frac{\Delta[CO_2]}{\Delta t} \qquad = \frac{\Delta[NO]}{\Delta t}$$

Since, nitrogen dioxide is a deep reddish brown gas, the rate of this reaction can be followed more easily by measuring the change in the intensity of colour in the gaseous mixture in a given interval of time.

2. Reactions involving different stoichiometric coefficients of reactants and products.

Consider another gaseous reaction between hydrogen and iodine to give hydro-iodic acid.

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)$$

The rate of this reaction can also be given in terms of rate of disappearance of one of the reactants H_2 or I_2 or in terms of the rate of formation of HI.

Now, in the present case, as the reactants (H_2 and I_2) and products (HI) have ***different stoichiometric coefficients***, this means that for every mole of H_2 or I_2 reacting we get two moles of HI. Thus, the rate of formation of HI will be twice the rate of disappearance or H_2 or I_2. Now in order to avoid the difference in the two rates, *i.e.*, to get a unique value of the reaction rate irrespective of the species selected, we divide the rate of change of concentration by the stoichiometric coefficient of reactant or product involved in the reaction. Thus, we have

$$\text{Rate of reaction} = -\frac{\Delta[H_2]}{\Delta t} = -\frac{\Delta[I_2]}{\Delta t} = \frac{1}{2}\frac{\Delta[HI]}{\Delta t}$$

Similarly, for a hypothetical reaction,

$$aA + bB \longrightarrow cC + dD$$

$$\text{Rate of reaction} = -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$$

Units of Rate of Reaction

As concentration of substance is expressed in mol L^{-1} and the time is expressed in seconds or minutes or hours the units for reaction rate, therefore, are **moles litre^{-1} sec^{-1}** or **moles litre^{-1} min^{-1}** or **moles litre^{-1} hr^{-1}**. For gaseous reactions, sometimes the concentrations of reactants and products are given in terms of partial pressures. Since pressure is expressed in atmospheres, therefore, the units of rate of reaction will be **atm min^{-1}** or **atm sec^{-1}** or **atm hr^{-1}**.

The partial pressure of any gaseous component can be calculated as

(*i*) From ideal gas equation, $pV = nRT$ or $p = \frac{nRT}{V} = \frac{w}{V}\frac{RT}{M} = \frac{dRT}{M}$

(*ii*) From the expression, $p = P_{Total} \times$ mole fraction of gas in question.

The partial pressure can also be converted into units of concentration, *i.e.*, moles per litre, by using the following equation :

$$pV = nRT \quad \text{or} \quad p = \frac{n}{V}RT = cRT \quad \text{or} \quad C = \frac{p}{RT}.$$

Example 6.1. *Describe the relationship between rate of reaction, rate of disappearance of X, Y and rate of appearance of X_2Y_3 in the reaction, $2X + 3Y \longrightarrow X_2Y_3$.*

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Solution. Rate of reaction $= -\frac{\Delta[X]}{2\Delta t} = -\frac{\Delta[Y]}{3\Delta t} = \frac{\Delta[X_2Y_3]}{\Delta t}$.

Example 6.2. *A chemical reaction* $2A \rightleftharpoons 4B + C$ *in gas phase occurs in closed vessel. The concentration of B is found to increase by* 5×10^{-3} *mol* L^{-1} *in 10 seconds. Calculate*

(*i*) *Rate of appearance of B* (*ii*) *Rate of reaction and*

(*iii*) *Rate of disappearance of A.*

Solution. Rate of appearance of B $= \frac{\text{Increase in conc. of B}}{\text{Time taken}}$

$$= \frac{5 \times 10^{-3}\ (\text{mol L}^{-1})}{10\ (\text{sec})} = \mathbf{5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$$

Rate of reaction $= \frac{1}{4} \times$ Rate of appearance of B

$$= \frac{1}{4} \times 5 \times 10^{-4} = \mathbf{1.25 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}$$

$\frac{1}{2}$(Rate of disappearance of A) = rate of reaction

$\therefore$ Rate of disappearance of A $= 2 \times$ rate of reaction

$$= 2 \times 1.25 \times 10^{-4}\ \text{mol L}^{-1}\ \text{s}^{-1}$$

$$= \mathbf{2.5 \times 10^{-4}\ mol\ L^{-1}\ s^{-1}}.$$

REVIEW PROBLEMS

6.1. Express the rates of the following reactions in terms of the concentrations of reactants and products :

(*i*) $PCl_5 \longrightarrow PCl_3 + Cl_2$ (*ii*) $N_2 + 3H_2 \longrightarrow 2NH_3$

(*iii*) $2NO_2 + F_2 \longrightarrow 2NO_2F$ (*iv*) $2N_2O_5 \longrightarrow 4NO_2 + O_2$

(*v*) $2ICl(g) + H_2(g) \longrightarrow I_2(g) + 2HCl(g)$.

6.2. For the following gaseous reaction, $2NO_2 \longrightarrow 2NO + O_2$.

(*i*) Write the expressions for the rate of the reaction.

(*ii*) If the rate of decrease of concentration of NO_2 is $4.0 \times 10^{-13}\ s^{-1}$, what are corresponding rates of increase in NO and O_2 concentrations ?

6.3. The reaction, $2N_2O_5(g) \rightleftharpoons 4NO_2(g) + O_2(g)$, takes place in a closed flask. It is found that concentration of NO_2 increases by 20×10^{-3} mol L^{-1} in 5 seconds. Calculate the rate of the reaction and the rate of change of concentration of N_2O_5.

6.4. For the following reaction, $4NH_3(g) + 5O_2(g) \longrightarrow 4NO(g) + 6H_2O(g)$

if the rate expression in terms of disappearance of NH_3 is $\frac{-\Delta[NH_3]}{\Delta t}$, write the rate expression in terms of concentrations of O_2 and H_2O.

6.5. For a reaction, $2I^- + Cl_2(g) \longrightarrow I_2 + 2Cl^-$, if the initial concentration of I^- was 0.80 mol/litre and conc. after 20 minutes was 0.68 mol/litre, calculate the rate of disappearance of I^- and rate of appearance of I_2.

6.6. Dinitrogen tetraoxide (N_2O_4) decomposes into NO_2 according to the equation

$$N_2O_4(g) \rightleftharpoons 2NO_2(g)$$

If the pressure of N_2O_4 falls from 0.46 atm to 0.28 atm in 30 minutes, what is the rate of appearance of $NO_2(g)$?

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6.7. For the decomposition of dinitrogen pentoxide at 200°C,

$$N_2O_5(g) \longrightarrow N_2O_4(g) + \frac{1}{2}O_2(g),$$

if the initial pressure is 114 mm and after 25 minutes of reaction the total pressure of gaseous mixture is 133 mm, calculate the average rate of reaction in (*a*) atmosphere min^{-1} and (*b*) mol L^{-1} s^{-1}.

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Average Rate and Instantaneous Rate

So far, we have been dealing with the expressions in which the change in concentration of the reactants or products is divided by the time interval during which the change occurs. Such rate expressions give the *average rate* of a reaction as these have been devised by employing the concept of mechanical speed.

Thus, the expression :

$$\frac{\textit{Change in concentration}}{\textit{Time interval}} \textit{ i.e., } \frac{\Delta x}{\Delta t} \text{ simply gives us the } \textbf{average} \text{ rate of the reaction.}$$

However, the concept of mechanical speed, as employed above, cannot be used to measure the true rate of a chemical reaction. This is because of the fact that the rate calculated as such would be constant for the whole span of time for which it is calculated. But on the contrary, it is observed that the rate of reaction is not constant but varies with time. This is because the rate of reaction is dependent on the molar concentration of reactants. Since the concentrations of the reactants keep on falling with time, therefore, the rate of a reaction keeps on decreasing with time. Since rate of reaction goes on changing from one moment to another, therefore, it is more appropriate to express the rate of a reaction at a particular moment of time. Such a reaction rate is called ***instantaneous rate.*** For this purpose, the time interval (Δt) is made infinitesimally small so that the change of concentration in that time interval remains almost uniform. Alternatively, the average rate approaches the instantaneous rate as Δt becomes smaller and approaches zero.

Mathematically, instantaneous rate may be expressed by the expression $\frac{dx}{dt}$* instead of $\frac{\Delta x}{\Delta t}$. Here, dt is the infinitesimally small time interval and dx is the change in concentration of any of the species in time interval dt.

In other words, the expression $\Delta x/\Delta t$ becomes dx/dt as Δt approaches zero *i.e.*,

$$\left(\frac{\Delta x}{\Delta t}\right)_{\Delta t \to 0} = \frac{dx}{dt}$$

For example, the instantaneous rate expressions for the gaseous reaction

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

can be put as $$\textit{Instantaneous rate} = -\frac{1}{2}\frac{d[N_2O_5]}{dt} = \frac{1}{4}\frac{d[NO_2]}{dt} = \frac{d[O_2]}{dt}.$$

6.2. EXPERIMENTAL DETERMINATION OF REACTION RATE

The rate of a reaction is determined by measuring the concentration of any of the reactants or products after a definite interval of time. For this purpose any *measurable property* which is related to the concentration

*In differential calculus, when Δt becomes small and approaches zero, the ratio $\frac{\Delta x}{\Delta t}$ (average rate) may be replaced by the derivative $\frac{dx}{dt}$ which means rate of change of x with time 't'. It may be put as $\lim_{\Delta t \to 0} \frac{\Delta x}{\Delta t} = \frac{dx}{dt}$.

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of species participating in the reaction is selected and change in this property is measured as a function of time. The measurable property can be any of following such as change in volume, pressure, refractive index, pH, electrical conductivity or thermal conductivity, etc., depending upon the suitability of experimental conditions. A graph is then plotted between *concentration* and *time*. The rate of the chemical reaction is found by drawing a tangent to the curve at the point P (Fig. 6.1) corresponding to the desired moment of time. The slope of the tangent gives the rate of the reaction at that time.

$$\text{Rate of reaction} = \text{Slope of the tangent} = \frac{\Delta x}{\Delta t}$$

where, Δx and Δt are intercepts as shown in Fig. 6.1.

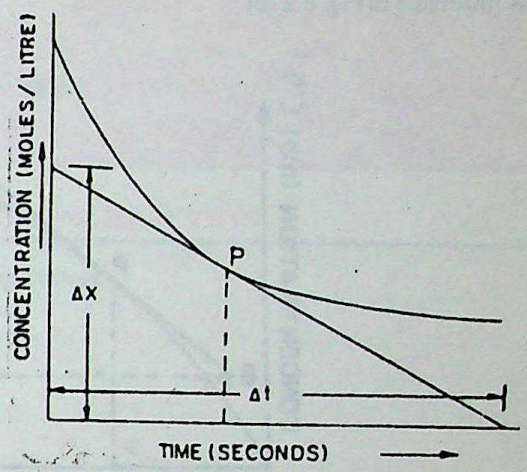

Fig. 6.1. Determination of rate of a reaction.

Calculation of average rate of the reaction. The average rate of the reaction at any instant of time can also be evaluated form the data of concentrations and time intervals as described below.

Here two equidistant points are taken with respect to the time at which the average rate is to be determined. The difference in concentrations corresponding to these points is calculated. This difference of concentration is then divided by the time interval between the selected equidistant points.

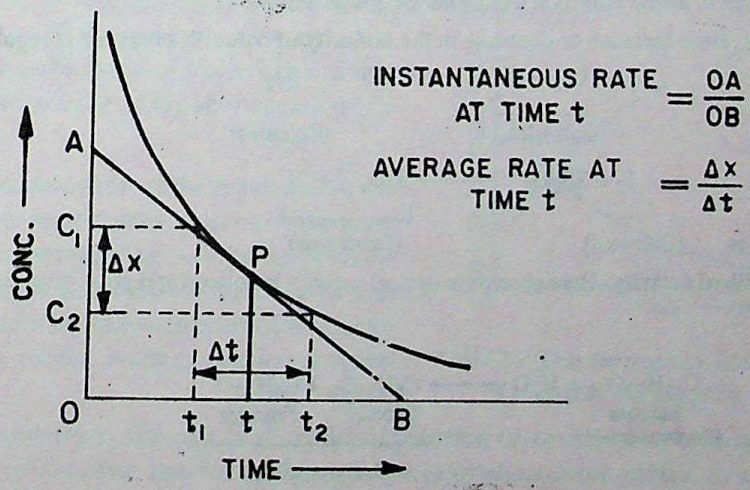

Fig. 6.2 (*a*)

For example, the average rate at time '*t*' can be calculated by measuring the change in concentration in the time interval from t_1 to t_2 (where t_1 and t_2 are two equidistant points about t as shown in Fig. 6.2 (*a*)).

$$\text{Thus, } \textit{average rate at time 't'} = \frac{C_2 - C_1}{t_2 - t_1} = \frac{\Delta x}{\Delta t}$$

On the other hand, the instantaneous rate at time t is given by the slope of the tangent at point P.

$$\textit{Instantaneous rate at time 't'} = \frac{OA}{OB}.$$

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It may be noted that instantaneous or average rate can also be determined by measuring the change in concentration or any other measurable property of product species as function of time and then plotting the graph between concentration *vs* time as illustrated in Fig. 6.2 (*b*).

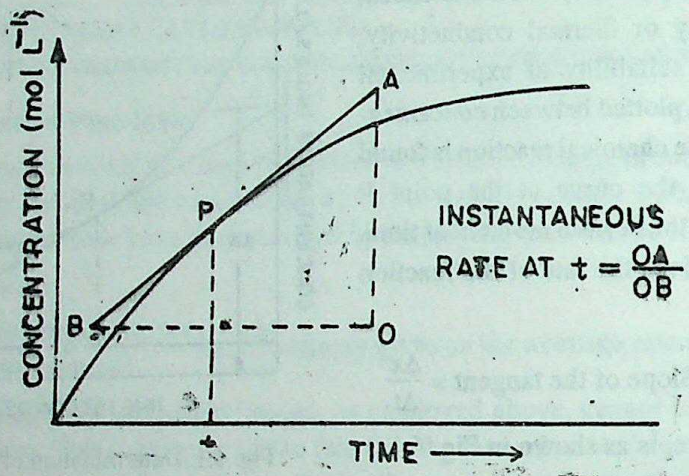

Fig. 6.2 (*b*)

Experimental Techniques of Measuring Reaction Rates

Experimental determination of reaction rates depends upon the nature of reaction under investigation. Rates, can be conveniently studied by measuring the suitable physical property of the system as a whole or of one of the constituent of the reaction. Some common examples are given below :

1. Colourimetry. Here increase or decrease in the intensity of colour is observed at regular intervals

$$\underbrace{Cl_2 + Br^-}_{\text{(Colourless)}} \longrightarrow 2Cl^- + \underset{\text{(Coloured)}}{Br_2}$$

$$\underset{\text{(Coloured)}}{I_2} + 2S_2O_3^{2-} \longrightarrow \underbrace{S_4O_6^{2-} + 2I^-}_{\text{(Colourless)}}$$

2. Change in optical activity. Here change in optical activity is noticed at regular intervals. Inversion of sugar is common example,

$$\underset{\substack{\text{Sucrose}\\ \text{(dextrorotatory)}}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underbrace{\underset{\textit{Glucose}}{C_6H_{12}O_6} + \underset{\textit{Fructose}}{C_6H_{12}O}}_{\text{(Laevorotatory)}}$$

3. pH measurement. In hydrolysis of ethyl acetate, the gradual increase in concentration of acetic acid is measured by measuring the pH of solution

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} C_2H_5OH + CH_3COOH$$

4. Change in pressure. Gradual increase or decrease of pressure is noticed in gaseous system.

$$SO_2(g) + Cl_2(g) \longrightarrow SO_2Cl_2(g)$$

5. Change in electrical conductance

$$[Co(NH_3)_5Cl_2] + H_2O \longrightarrow [Co(NH_3)_5Cl_2H_2O]^+ + Cl^-$$

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With the progress of reaction, the number of ions in the solution increase thereby gradual increase in conductance of the solution.

6. Measuring volume of one of the gaseous product

$$C_6H_5N_2^+Cl^- \longrightarrow C_6H_5Cl + N_2(g)$$

Here, gradual increase in volume of N_2 is measured.

6.3. FACTORS AFFECTING THE RATE OF A CHEMICAL REACTION

The rate of reactions in influenced by the following factors :

(*i*) *Concentration of the reactants,*
(*ii*) *Temperature of the reactants,*
(*iii*) *Nature of the reacting substances,*
(*iv*) *Presence of catalyst, and*
(*v*) *Exposure to radiations.*

6.4. EFFECT OF CONCENTRATION

When a chemical reaction occurs, the reactants change over to products. It is observed that with the passage of time the concentrations of reactants decrease while those of products increase. It is graphically shown in Fig. 6.3.

Now, if we assume that other factors are constant then the rate of a chemical reaction decreases with the decrease in concentration of the reactants. *For example, we find that a piece of wood burns at a much faster rate in oxygen than in air. It is because of higher concentration of O_2 in the former.*

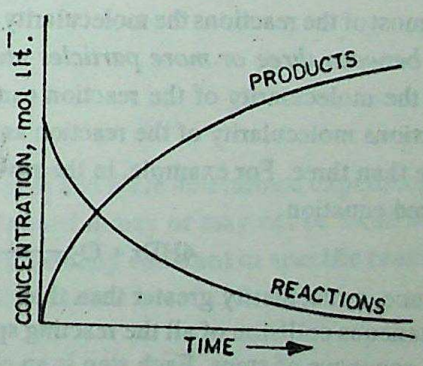

Fig. 6.3. Time dependence of the concentrations of reactants and products in a reaction.

The effect of concentration of the reactants on the reaction rate, at a constant temperature is given by the **Law of Mass Action.** This generalisation was given by Cato Guldberg and Peter Waage. It is a theoretical concept and gives a qualitative relationship between rates of reactions and the concentrations of the reacting species. It states that :

"At a given temperature, the rate of a chemical reaction is directly proportional to the product of molar concentrations of reacting species with each concentration term raised to the power equal to numerical coefficient of that species in the chemical equation.

Thus, for a hypothetical reaction ;

$$A + B \longrightarrow \text{Products}$$

The rate according to law of mass action is given as

Rate of reaction, $r \propto [A][B] = k[A][B]$

where [A] and [B] are the molar concentrations of the reactants A and B respectively and k is a constant of proportionality.

For any general hypothetical reaction,

$$aA + bB \longrightarrow cC + dD$$

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The rate of reaction according to law of mass action may be written as

$$\text{Rate} = k[A]^a[B]^b$$

Although the above rate expression has been written from the balanced chemical equation, yet it may or may not give the actual dependence of the reaction rate on concentrations of reacting species. The actual relationship between the concentrations of reacting species and the reaction rate is determined experimentally and is given by the expression called *rate law expression*. Before we take up the discussion of rate law let us study about molecularity and mechanism of the reaction.

Molecularity and Mechanism of Reaction

According to collision theory a chemical reaction takes place due to collisions between the particles of the reactants. *The number of reacting species (atoms, ions or molecules) which must collide simultaneously in order to bring about the chemical reaction is called* **molecularity** *of the reaction.* The molecularity of the reaction can be 1, 2 or 3. For example, the decomposition of ammonium nitrite is a **unimolecular** reaction.

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Similarly, the reaction involving simultaneous collision between *two species* is a **bimolecular** reaction. For example, dissociation of HI is a bimolecular reaction.

$$2HI(g) \longrightarrow H_2(g) + I_2(g)$$

In the same way, the reaction between NO and O_2 is a **trimolecular** reaction.

$$2NO + O_2 \longrightarrow 2NO_2$$

In most of the reactions the molecularity does not exceed three. It is because the *chances of simultaneous collisions between three or more particles* are rare*. In general, for ***elementary reactions*** *i.e.*, single step reactions, the molecularity of the reaction can be obtained from balanced chemical equation. However, in many reactions molecularity of the reaction as obtained from the balanced chemical equation may come out to be more than three. For example, in the reaction between HBr and O_2 the molecularity is *five* as given by the balanced equation.

$$4HBr + O_2 \longrightarrow 2H_2O + 2Br_2$$

Since, molecularity greater than three is not possible, therefore, the above reaction does not involve the simultaneous collision of all the reacting species in a single step. In fact, such chemical reactions proceed through a sequence of steps. Each step is an elementary step and involves the simultaneous collision of two or three species only. Such ***chemical reactions which proceed through more than one steps are termed as complex reactions.***

*The detailed description of various steps** of the chemical reaction* is called **mechanism of the reaction.** For example, the above reaction occurs by the following steps :

$$\begin{array}{l} HBr + O_2 \longrightarrow HOOBr \\ HOOBr + HBr \longrightarrow 2HOBr \\ \underline{HOBr + HBr \longrightarrow H_2O + Br_2] \times 2} \\ 4HBr + O_2 \longrightarrow 2H_2O + 2Br_2 \end{array}$$

*The logic has been concluded on the basis of our daily experience gathered from roads where we seldom come across accidents in which three or more vehicles are involved simultaneously. As the chemical collisions are considered to be analogous to vehicular accidents, similar conclusions are therefore drawn there too.

**The stepwise reactions are not necessarily observable ; they are merely proposed pathways from reactants to products which logically fit into all the available experimental data.

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It is clear from the above discussion that a complex reaction occurs in two or more steps. ***The term molecularity of overall reaction has no significance in this case.*** Here a curious question arises in our minds regarding the expression that shall be employed to express the rates of such reactions *i.e.*, will it be given by the overall balanced equation or by some individual step ? The answer of this question follows from the following discussion.

Rate Law or Rate Equation

In complex reactions the rate expression written on the basis of the overall balanced equation has no significance at all. It merely represents a theoretical expression. The true rate expression for such complex reactions can be evaluated on the basis of the experimental data only. For example, in the reaction between NO_2 and F_2 to yield nitryl fluoride (NO_2F),

$$2NO_2(g) + F_2(g) \longrightarrow 2NO_2F(g)$$

the expected rate expression is

$$\text{rate} = k\,[NO_2]^2\,[F_2]$$

But it is experimentally found that the rate of this reaction is proportional to the product of single concentration term of NO_2 and F_2. Thus, experimental rate of the reaction is given as

$$\text{rate} = k[NO_2]\,[F_2].$$

Such a mathematical expression that gives the true rate of a reaction in terms of concentration of the reactants, which actually influence the rate, is called **rate law.**

In general, for any hypothetical reaction,

$$aA + bB \longrightarrow cC + dD$$

The rate law expression may be written as :

$$\text{rate} = k\,[A]^m\,[B]^n \qquad ...(6.1)$$

In the above rate law expression, the numerical values of m and n are determined experimentally and cannot be deduced from the balanced equation. The values of m and n may or may not be same as a and b. The constant k in the rate law expression is called **rate constant, velocity constant** or **specific reaction rate.** Now, if the concentration of each of the reactants involved in the reaction is unity,

i.e., $[A] = [B] = 1 \text{ mol L}^{-1}$, then

$$\text{rate} = k \times 1 \times 1 = k$$

Thus, the **rate constant** of a reaction at given temperature may be defined as ***the rate of the reaction when the concentration of each of the reacting species is unity.***

Some of the **characteristics of rate constant** are :

(*i*) The value of k is different for different reactions.

(*ii*) It is a measure of intrinsic rate of reaction. This means larger the value of k, faster will be the reaction. Similarly, small value of k reflects slower reaction.

(*iii*) At a fixed temperature, the value of k is constant and characteristic of the reaction.

(*iv*) For a particular reaction, k is independent of concentration but depends on temperature.

The important differences between the ***rate*** of the reaction and ***rate constant*** of the reaction are being given as follows in tabular form.

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Rate of reaction	*Rate constant of reaction*
1. It is the speed at which the reactants are converted into the products at any moment of time.	1. It is constant of proportionality in the rate law expression.
2. It depends upon the concentration of reactant species at that moment of time.	2. It refers to the rate of reaction at the specific point when concentration of every reacting species is unity.
3. It generally decreases with the progress of reaction.	3. It is constant and does not depend on the progress of the reaction.

Rate controlling step

As pointed out that the complex reaction proceeds through more than one steps. An important question arises as to which of these steps can be used to write the rate expression. Out of various steps of the reaction the slowest step will decide the rate of overall reaction because the reaction cannot take place faster than the slowest step Thus, the *slowest step of the complex reaction* is called the **rate controlling step** or **rate determining step.**

The rate law expression of a complex reaction gives an indication about the slowest step in the mechanism of the reaction. For example, for the decomposition of nitrous oxide

$$2N_2O \longrightarrow 2N_2 + O_2$$

the rate law expression is found to be,

$$\text{Rate} = k\,[N_2O]$$

Since the rate of the reaction depends only upon single power of N_2O, it indicates the only one molecule of N_2O is involved in the slow step. Thus, with this knowledge and chemical intuition a possible mechanism of the reaction may be proposed as :

$$N_2O \xrightarrow{\textit{Slow step}} N_2 + O$$

$$N_2O + O \xrightarrow{\textit{Fast step}} N_2 + O_2$$

$$2N_2O \longrightarrow 2N_2 + O_2 \quad \text{...Overall reaction}$$

The above postulated mechanism is consistent with the rate law expression.

It must be noted here that there is no way to verify the absolute validity of the proposed mechanism. All we can do is to postulate a mechanism that is consistent with experimental data. If further investigations reveal information that is inconsistent with postulated mechanism, it has to be modified accordingly so as to explain all the observations.

Example 6.3. *For a reaction,* $2NO_2 + F_2 \longrightarrow 2NO_2F$ *the experimental rate law is* $r = k[NO_2]\,[F_2]$. *Propose the mechanism of the reaction.*

Solution. The rate law is $r = k[NO_2]\,[F_2]$

Since rate law is proportional to single power of NO_2 and single power of F_2 it implies that only one molecule of NO_2 and one molecule of F_2 are involved in the slow step. Thus, the various steps are :

$$NO_2 + F_2 \longrightarrow NO_2F + F \quad \text{...(slow)}$$

$$NO_2 + F \longrightarrow NO_2F \quad \text{...(fast)}$$

$$2NO_2 + F_2 \longrightarrow 2NO_2F \quad \text{...(Overall reaction)}$$

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Example 6.4. *The reaction,* $2NO + Br_2 \longrightarrow 2NOBr$ *proceeds by the following mechanism :*

$$(i)\quad NO + Br_2 \underset{fast}{\overset{step\ I}{\rightleftharpoons}} NOBr_2 \qquad (ii)\ NOBr_2 + NO \underset{fast}{\overset{step\ II}{\longrightarrow}} 2NOBr$$

Suggest a rate law consistent with the mechanism.

Solution. As the slowest step is the rate determining step, therefore the rate law is

$$r = k\,[NOBr_2]\,[NO]$$

Now since $NOBr_2$ is an intermediate its concentration can be calculated from step I as a follows

$$K = \frac{[NOBr_2]}{[NO]\,[Br_2]} \qquad [K = \text{Eq. constant}]$$

or $$[NOBr_2] = K\,[NO]\,[Br_2]$$

Substituting this value in above equation

$$r = k.\,K\,[NO]\,[Br_2]\,[NO]$$

or $$\text{rate} = k'\,[NO]^2\,[Br_2] \qquad [\because\ k.K = \text{constant } k']$$

$\therefore$ Rate law is $$\text{rate} = k'\,[NO]^2\,[Br_2].$$

REVIEW PROBLEMS

6.8. The reaction $2NO_2Cl \longrightarrow 2NO_2 + Cl_2$ has the rate law : $r = k[NO_2Cl]$. What is its mechanism ?

6.9. The rate expression for a chemical reaction

$$(CH_3)_3\,C{-}Cl + OH^- \longrightarrow (CH_3)_3\,C{-}OH + Cl^- \text{ is}$$

$r = k\,[(CH_3)_3\,C{-}Cl]$. Propose the mechanism.

6.10. If thermal decomposition of dinitrogen pentaoxide is written as

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

and the rate law is $r = k\,[N_2O_5]$. Propose the mechanism of reaction.

6.11. The rate expression for a chemical reaction

$$4HBr(g) + O_2(g) \longrightarrow 2H_2O(g) + 2Br_2(g) \text{ is rate} = k\,[HBr]\,[O_2].$$

What is the probable mechanism of the reaction ?

6.12. If the reaction between H_2 and I_2 to produce HI takes place by the following mechanism then what is the rate law expression ?

$$I_2 \rightleftharpoons 2I\ (fast)$$

$$I + H_2 \rightleftharpoons IH_2\ (fast)$$

$$IH_2 + I \longrightarrow 2HI\ (slow)$$

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Order of Reaction

It is an important parameter for every chemical reaction. It is always determined experimentally and cannot be written from the balanced chemical equation. It refers to the number of reacting particles whose concentration terms determine the reaction rate.

It may be defined as

the sum of powers or exponents to which the concentration terms are raised in the rate law expression.

For example, for a hypothetical reaction,

$$aA + bB \longrightarrow \text{Products}$$

it the rate law expression for this reactions is,

$$\text{Rate} = k[A]^m [B]^n$$

Then, **order** of the reaction is equal to **(m + n)**. These powers or exponents, *i.e.*, *m* and *n* have no relation to the stoichiometric coefficients *a* and *b* of the balanced chemical equation. Order of the reaction with respect to A is *m* and that with respect to B is *n*. If the sum of the power is equal to *one*, the reaction is called *first order reaction*. If the sum of the powers is *two* or *three*, the reaction is *second order* or *third order* reaction respectively. *The order of a reaction can also be zero or fractional.*

For illustration, a few examples are given below :

(*i*) Nitrous oxide (N_2O) decomposes as :

$$2N_2O(g) \longrightarrow 2N_2(g) + O_2(g)$$

The rate law expression for this reaction is

$$\text{Rate} = k\,[N_2O]\,; \qquad \text{Order} = 1$$

Therefore, it is a ***first order*** reaction.

(*ii*) For the reaction,

$$H_2(g) + I_2(g) \longrightarrow 2HI(g)\ ;\ \text{The rate law is}$$

$$\text{Rate} = k[H_2][I_2]\ ;\ \text{Order} = 1 + 1 = 2$$

So, it is a ***second order*** reaction.

(*iii*) The reaction between nitric oxide and oxygen is an example of ***third order*** reaction.

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)\ ;\ \text{The rate law is}$$

$$\text{Rate} = k[NO]^2[O_2]\ ;\ \text{Order} = 2 + 1 = 3.$$

(*iv*) The reaction between hydrogen and bromine to form hydrogen bromide has ***fractional order***

$$H_2(g) + Br_2(g) \longrightarrow 2HBr(g)\ ;\ \text{The rate law is}$$

$$\text{Rate} = k\,[H_2][Br_2]^{1/2}\ ;\quad \text{Order} = 1 + \tfrac{1}{2} = \tfrac{3}{2}.$$

(*v*) Decomposition of ammonia over platinum or gold is a ***zero order reaction***

$$2NH_3 \xrightarrow{\text{Platinum}} N_2 + 3H_2$$

Rate law is :

$$r = k\,[NH_3]^0$$

In this reaction, metal acts as catalyst. At sufficiently high pressure the surface of metal is completely covered by the ammonia molecules. Therefore, further increase in pressure (concentration) of NH_3 does not change the reaction rate. It is thus, independent of concentration and is zero order reaction. For the better understanding, the *concentration* vs *time* graph and *rate* vs *time* graph for *zero order reactions* are being given below.

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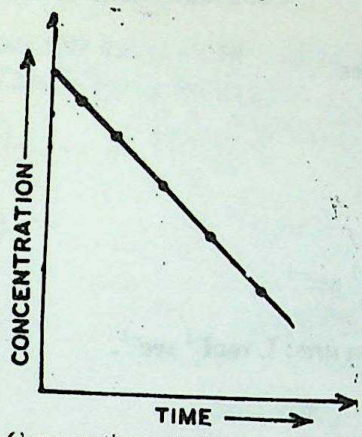
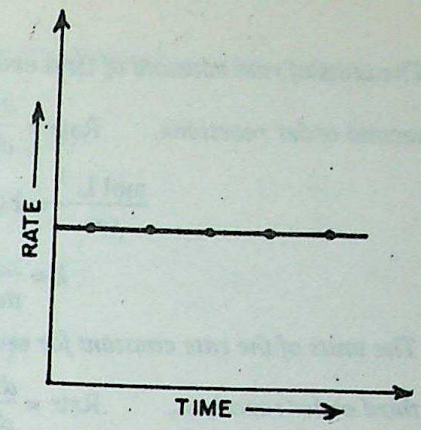


Conc. *vs* time graph for zero order



Rate *vs* time graph for zero order reaction

The other examples of reactions with different orders are given in Table 6.1.

Table 6.1. Examples of Reactions having Different Orders

Examples	*Rate law*	*Order*
First order reactions		
$2H_2O_2 \longrightarrow 2H_2O + O_2$	$r = k\,[H_2O_2]$	1
$C_2H_5Cl \longrightarrow C_2H_4 + HCl$	$r = k\,[C_2H_5Cl]$	1
$2N_2O_5 \longrightarrow 4NO_2 + O_2$	$r = k\,[N_2O_5]$	1
$SO_2Cl_2 \longrightarrow SO_2 + Cl_2$	$r = k\,[SO_2Cl_2]$	1
Second order reactions		
$NO + O_3 \longrightarrow NO_2 + O_2$	$r = k\,[NO][O_3]$	2
$2NO_2 \longrightarrow 2NO + O_2$	$r = k\,[NO_2]^2$	2
$H_2 + I_2 \longrightarrow 2HI$	$r = k\,[H_2][I_2]$	2
$CH_3CO_2C_2H_5 + OH^- \longrightarrow CH_3CO_2^- + C_2H_5OH$	$r = k\,[CH_3CO_2C_2H_5][OH^-]$	2
Third order reactions		
$2NO + O_2 \longrightarrow 2NO_2$	$r = k\,[NO]^2[O_2]$	3
$2NO + Br_2 \longrightarrow 2NOBr$	$r = k\,[NO]^2[Br_2]$	3
Fractional order reactions		
$CO + Cl_2 \longrightarrow COCl_2$	$r = k\,[CO]^2[Cl_2]^{1/2}$	2.5
$COCl_2 \longrightarrow CO + Cl_2$	$r = k\,[COCl_2]^{3/2}$	1.5
$CH_3CHO \longrightarrow CH_4 + CO$	$r = k\,[CH_3CHO]^{3/2}$	1.5
Zero order reactions		
$2NH_3 \xrightarrow{Pt} N_2 + 3H_2$	$r = k\,[NH_3]^0$	0

Units of rate constant. The rate constant k has different units for reactions having different orders. For *first order reactions,*

$$\text{Rate} = \frac{dx}{dt} = k\,[A]$$

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k\,.\,\text{mol L}^{-1} \quad \text{or} \quad k = \frac{1}{\text{sec}} = \text{sec}^{-1}.$$

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∴ *The units of rate constant of* **first order reaction** *are* : sec^{-1}.

For *second order reactions*, $\text{Rate} = \frac{dx}{dt} = k[A]^2$

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k\,(\text{mol L}^{-1})^2$$

or $$k = \frac{1}{\text{mol L}^{-1}\ \text{sec}} = \text{L mol}^{-1}\ \text{sec}^{-1}.$$

∴ *The units of the rate constant for* **second order reaction** *are* : $L\ mol^{-1}\ sec^{-1}$.

For *third order reactions*, $\text{Rate} = \frac{dx}{dt} = k\,[A]^3$

$$\frac{\text{mol L}^{-1}}{\text{sec}} = k\,(\text{mol L}^{-1})^3$$

or $$k = \frac{1}{\text{sec mol}^2\,.\,\text{L}^{-2}} = \text{L}^2\ \text{mol}^{-2}\ \text{sec}^{-1}.$$

∴ *The units of rate constant for* **third order reaction** *are* : $L^2\ mol^{-2}\ sec^{-1}$.

> In general, for a reaction of **nth order**, the units of rate constant are $(\text{mol L}^{-1})^{1-n}\ \text{sec}^{-1}$
> And for gaseous reaction of **nth order**, k has units of $(\text{atm})^{1-n}\ \text{sec}^{-1}$.

Pseudo First Order Reactions

Many a times the reaction of higher order follows the kinetics of first order under special conditions. Such reactions are called **pseudo first order reactions.** For example, consider a hypothetical reaction

$$A + B \longrightarrow AB$$

Now, if concentration of B is large enough so that it does not change appreciably during the reaction, then its rate will depend on the single concentration term and it will follow the kinetics of the first order. Acidic hydrolysis of ethyl acetate is a common example of this type.

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

Here, the rate of reaction is given by expression

$$r = k\,[CH_3COOC_2H_5]$$

Since concentration of H_2O is quite large and does not change appreciably, therefore, it does not appear in the rate law.

Differences between molecularity and order of a reaction

Molecularity	*Order*
1. It is the number of reacting species undergoing simultaneous collision in the reaction.	It is sum of the powers of the concentration terms in the rate law expression.
2. It is a theoretical concept.	It is determined experimentally.
3. It can have integral values only.	It can have fractional values also.
4. It cannot be zero.	It can be zero.
5. It does not tell us anything about the mechanism of the reaction.	It tells us about the slowest step in the mechanism and hence gives some clue about mechanism of the reaction.

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Example 6.5. *State the order w.r.t. each reactant, order of overall reaction and units of rate constant in each of the following reactions.*

(*i*) $$H_2O_2 + 3I^- + 2H^+ \longrightarrow 2H_2O + I_3^-\,(aq)$$

$$rate = k\,[H_2O_2][I^-]$$

(*ii*) $$CO + Cl_2 \longrightarrow COCl_2$$

$$rate = k\,[CO]^2[Cl_2]^{1/2}$$

(*iii*) $$CH_3CHO \longrightarrow CH_4 + CO$$

$$rate = k\,[CH_3CHO]^{3/2}$$

(*iv*) $$2NO + Br_2 \longrightarrow 2NOBr$$

$$rate = k\,[NO]^2[Br_2]$$

Sol. (*i*) $$\text{Rate} = k\,[H_2O_2][I^-]$$

Order w.r.t. H_2O_2 = **1** ; Order w.r.t. I^- = **1**

Overall order = **2**

Units of $k = (\text{mol L}^{-1})^{1-2}\,\text{s}^{-1} = \textbf{mol}^{-1}\,\textbf{L s}^{-1}$

(*ii*) $$\text{Rate} = k\,[CO]^2[Cl_2]^{1/2}$$

Order w.r.t. to CO = **2** ; Order w.r.t. Cl_2 = **1/2**

Overall order = **2.5**

Units of $k = (\text{mol L}^{-1})^{1-2.5}\,\text{s}^{-1} = \textbf{mol}^{-3/2}\,\textbf{L}^{3/2}\,\textbf{s}^{-1}$

(*iii*) $$\text{Rate} = k\,[CH_3CHO]^{3/2}$$

Order w.r.t. to CH_3CHO = **1.5** ; Overall order = **1.5**

Units of $k = (\text{mol L}^{-1})^{1-1.5}\,\text{s}^{-1} = \textbf{mol}^{-1/2}\,\textbf{L}^{1/2}\,\textbf{s}^{-1}$

(*iv*) $$\text{Rate} = k\,[NO]^2\,[Br_2]$$

Order w.r.t. NO = **2** ; Order w.r.t. Br_2 = **1**

Overall order = **3**

Units of $k = (\text{mol L}^{-1})^{1-3}\,\text{s}^{-1} = \textbf{mol}^{-2}\,\textbf{L}^{2}\,\textbf{s}^{-1}$.

Experimental Determination of Order of Reaction

The following methods are employed to determine the *rate law, rate constant and order of reaction.*

1. **Graphical method.** This method is used to determine the rate law of the reaction which involves only *one reactant species*. The various steps involved are :

(*i*) The concentrations of reacting substance are determined at different time intervals by some suitable method.

(*ii*) A graph is plotted between concentration and time.

(*iii*) For the plot of *concentration* vs. *time*, the instantaneous rates corresponding to different concentrations are determined by drawing tangents to the curve and subsequently calculating their slopes as discussed in section 6.2.

(*iv*) Different graphs are now plotted as follows between :

(*a*) *reaction rate* vs. *concentration* or

(*b*) *reaction rate* vs. *(concentration)*^{2} or in general,

(*c*) *reaction rate* vs. *(concentration)*^{n}, where n = 1, 2, 3 and so on.

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If a straight line is obtained in the first case, it means the rate is directly proportional to concentration of the reactant. This in turn means that the rate law is given as,

$$\text{rate} = k\,[\text{Reactant}]$$

and therefore its order in *one*.

Similarly, if a straight line is obtained in second case, then

$$\text{rate} = k\,[\text{Reactant}]^2$$

and its order is *two*.

Let us explain the above method, in details, by taking the example of decomposition of dinitrogen pentaoxide,

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

As the above reaction involves gaseous reactants and products, therefore, it is convenient to observe the changes in the pressure, accompanying the reaction. From the measured values of total pressure, first the partial pressure of N_2O_5 is calculated and then the concentration in moles per litre of N_2O_5 is determined. The molar concentrations of N_2O_5 at different time intervals so obtained are given in Table 6.2.

Table 6.2. Concentration—Time Data for Decomposition of $N_2O_5(g)$

Time (min)	*$[N_2O_5]$ (mo L^{-1})*
0	1.72×10^{-2}
10	1.13×10^{-2}
20	0.84×10^{-2}
30	0.62×10^{-2}
40	0.46×10^{-2}
50	0.35×10^{-2}
60	0.26×10^{-2}
70	0.19×10^{-2}
80	0.14×10^{-2}

Thereafter, the rates for reactions (Table 6.3) at different junctures are obtained by calculating the slope of the tangent of the curve in Fig. 6.4. (*obtained by plot of $[N_2O_5]$ as a function of time*).

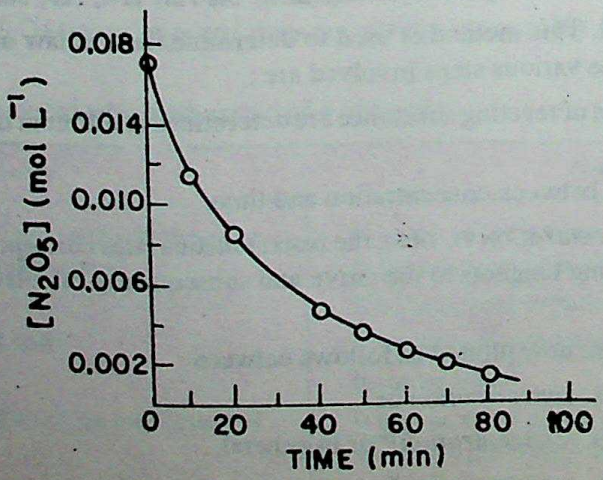

Fig. 6.4. Concentration of N_2O_5 as a function of time.

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Table 6.3. Rate Data for Decomposition of $N_2O_5(g)$

$[N_2O_5]$ (mol L^{-1})	Rate (mol L^{-1} min^{-1})
1.13×10^{-2}	34×10^{-5}
0.84×10^{-2}	25×10^{-5}
0.62×10^{-2}	18×10^{-5}
0.46×10^{-2}	13×10^{-5}
0.35×10^{-2}	10×10^{-5}
0.26×10^{-2}	8×10^{-5}
0.19×10^{-2}	6×10^{-5}
0.14×10^{-2}	4×10^{-5}

Now two graphs are drawn by plotting (*i*) *rate* against *concentration* of N_2O_5 *i.e.*, $[N_2O_5]$ as shown in Fig. 6.5 and (*ii*) rate against square of concentration of N_2O_5 *i.e.*, $[N_2O_5]^2$ as shown in Fig. 6.6. We find that a straight line is obtained in the first case which means that

$$\text{rate} \propto [N_2O_5]$$

and thus, the *rate law expression* is given as

$$\text{rate} = k\,[N_2O_5]$$

Also, the value of *rate constant k*, evaluated from rate data (Table 6.3) is,

$$k = \frac{\text{rate}}{[N_2O_5]} = 3.0 \times 10^{-2}\ \text{min}^{-1}$$

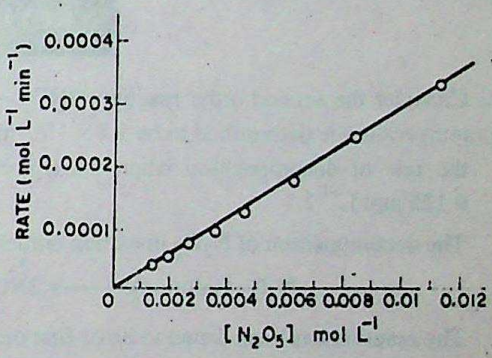

Fig. 6.5. Rate of decomposition of N_2O_5 as a function of $[N_2O_5]$.

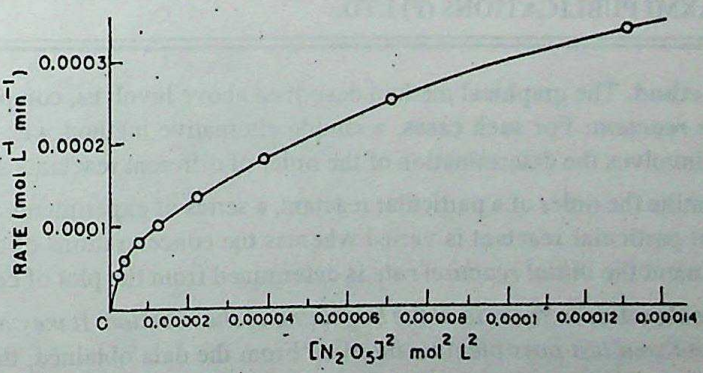

Fig. 6.6. Rate of decomposition of N_2O_5 as a function of $[N_2O_5]^2$.

Example 6.6. *If the decomposition of nitrogen (V) oxide* $2N_2O_5 \longrightarrow 4NO_2 + O_2$, *following a first order kinetics,*

(*i*) *Calculate the rate constant for a 0.04 M solution, if the instantaneous rate is* 1.4×10^{-6} *mol* L^{-1} s^{-1}.

(*ii*) *Also calculate the rate of reaction when the concentration of* N_2O_5 *is 1.20 M.*

(*iii*) *What concentration of* N_2O_5 *would give a rate of* 2.45×10^{-5} *mol* L^{-1} s^{-1} ?

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Solution. (*i*) As the given reaction is of first order, therefore,

$$\text{rate} = k\,[N_2O_5]$$

or

$$k = \frac{\text{rate}}{[N_2O_5]} = \frac{1.4 \times 10^{-6}}{0.04} \qquad [M = \text{Conc. in mol } L^{-1}]$$

$$= \mathbf{3.5 \times 10^{-5}\ s^{-1}}.$$

(*ii*) Now if the concentration of N_2O_5 is 1.20 M, then

$$\text{rate} = k\,[N_2O_5]$$

$$= 3.5 \times 10^{-5} \times 1.20 = \mathbf{4.2 \times 10^{-5}\ mol\ L^{-1}\ s^{-1}}.$$

(*iii*) To obtain concentration of N_2O_5 when the rate is 2.45×10^{-5} mol L^{-1} s^{-1}, we note that

$$[N_2O_5] = \frac{\text{Rate}}{k} = \frac{2.45 \times 10^{-5}}{3.5 \times 10^{-5}} = \mathbf{0.7\ mol\ L^{-1}\ or\ 0.7\ M.}$$

REVIEW PROBLEMS

6.13. Consider the second order reaction, $2NO_2 \longrightarrow 2NO + O_2$. The rate of decomposition of NO_2 at a certain temperature is determined to be 1.4×10^{-3} mol L^{-1} min^{-1} at NO_2 concentration of 0.500 mol L^{-1}. What will be the rate of decomposition when the concentration of NO_2 is 0.250 M and when the concentration of NO_2 is 0.125 mol L^{-1} ?

6.14. The decomposition of N_2O_5 in carbon tetrachloride solution has been investigated

$$N_2O_5\,(\text{solution}) \longrightarrow 2NO_2\,(\text{solution}) + \tfrac{1}{2}O_2(g)$$

The reaction has been found to be of first order in N_2O_5 with a first order rate constant 6.2×10^{-6} s^{-1}. Calculate the rate of the reaction when (*a*) $[N_2O_5] = 1.25$ mol L^{-1} and (*b*) $[N_2O_5] = 1.5$ mol L^{-1}. What concentration of N_2O_5 would give a rate of 2.4×10^{-5} mol L^{-1} s^{-1} ?

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5. Initial rate method. The graphical method described above involves, complications if the reaction involves *more than one reactant*. For such cases, a simple alternative method, *i.e., Initial Rate Method* is employed. The method involves the determination of the order of different reactants separately.

In order to determine the order of a particular reactant, a series of experiments are performed in which the concentration of that particular reactant is varied whereas the concentrations of other reactants are kept constant. In each experiment the *initial reaction rate* is determined from the plot of *conc. vs. time.*

Initial reaction rate refers to the *rate at the beginning of the reaction. It may also be taken as the rate over the first feasible and smallest possible time interval.* From the data obtained, the order with respect to particular reactant is calculated. *(See example 6.7-6.9)*

The same procedure is then repeated by devising another set of experiments of the same reaction in which the concentration of the second reactant is varied whereas those of others are kept constant. Then, by a similar method as discussed above, the initial rates for different experimental runs and hence the order with respect to the second reactant is determined.

The results then put together give the rate law expression.

Let us illustrate it by an example given below.

Example 6.7. *For the reaction between nitric oxide (NO) and hydrogen (H_2),*

$2NO + 2H_2 \longrightarrow N_2 + 2H_2O$, *the following rate data were obtained :*

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Experiment	*Initial concentrations* ($mol\ L^{-1}$)		*Initial rate* ($mol\ L^{-1}\ s^{-1}$)
	[NO]	*[H_2]*	
1	*0.20*	*0.20*	3.20×10^{-3}
2	*0.40*	*0.20*	1.28×10^{-2}
3	*0.20*	*0.40*	6.40×10^{-3}

(*i*) *Write the most probable rate equation for the reaction and*

(*ii*) *calculate the value of rate constant, k.*

Solution. The expression for the initial rate of this reaction will be

$$\text{Initial rate} = k[NO]^x\,[H_2]^y.$$

The values of initial rates and initial concentrations are substituted in the above expression and then by simple mathematical manipulation x and y are evaluated.

$$\text{For Exp. 1, } 3.20 \times 10^{-3} = k\,[0.20]^x\,[0.20]^y \quad ...(i)$$

$$\text{For Exp. 2, } 1.28 \times 10^{-2} = k[0.40]^x\,[0.20]^y \quad ...(ii)$$

$$\text{For Exp. 3, } 6.40 \times 10^{-3} = k[0.20]^x\,[0.40]^y \quad ...(iii)$$

Evaluation of x. Divide equation (*ii*) by eq. (*i*)

$$\frac{1.28 \times 10^{-2}}{3.20 \times 10^{-3}} = \frac{k[0.40]^x\,[0.20]^y}{k[0.20]^x\,[0.20]^y}$$

$$\frac{12.8}{3.2} = \left(\frac{0.40}{0.20}\right)^x$$

$$4.0 = (2.0)^x$$

$$(2.0)^2 = (2.0)^x$$

$$\therefore \quad x = \mathbf{2.}$$

Evaluation of y. Divide eq. (*iii*) by eq. (*i*),

$$\frac{6.40 \times 10^{-3}}{3.20 \times 10^{-3}} = \frac{k[0.20]^x\,[0.40]^y}{k[0.20]^x\,[0.20]^y}$$

$$(2.0)^1 = (2.0)^y$$

$$\therefore \quad y = \mathbf{1.}$$

(*i*) Thus, the rate equation is $r = k[NO]^2[H_2]$.

(*ii*) Also the value of rate constant $k = \dfrac{\text{rate}}{[NO]^2\,[H_2]} = \dfrac{3.20 \times 10^{-3}}{0.20 \times 0.20 \times 0.20} = \mathbf{0.4\ mol^{-2}\ L^2\ s^{-1}}$.

Example 6.8. *The experimental data for the reaction*

$$2A + B_2 \longrightarrow 2AB \text{ is}$$

Experiment	*[A]* ($mol\ L^{-1}$)	*[B_2]* ($mol\ L^{-1}$)	*Initial Rate*
1	*0.50*	*0.50*	1.6×10^{-4}
2	*0.50*	*1.00*	3.2×10^{-4}
3	*1.00*	*1.00*	3.2×10^{-4}

Write the rate law equation. (Roorkee Ent. 1991)

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Solution. Let the rate law be $r = k\,[A]^x[B_2]^y$

Now,
$$r_1 = 1.6 \times 10^{-4} = k[0.50]^x[0.50]^y \quad ...(i)$$
$$r_2 = 3.2 \times 10^{-4} = k[0.50]^x\,[1.00]^y \quad ...(ii)$$
$$r_3 = 3.2 \times 10^{-4} = k[1.00]^x\,[1.00]^y \quad ...(iii)$$

Divide (*ii*) by (*i*),
$$\frac{r_2}{r_1} = \frac{k(0.50)^x\,(1.00)^y}{k(0.50)^x\,(0.50)^y} = \frac{3.2 \times 10^{-4}}{1.6 \times 10^{-4}}$$
$$\left(\frac{1.00}{0.50}\right)^y = 2 \quad \text{or} \quad 2^y = 2 \quad \text{or} \quad y = 1$$

Now divide (*iii*) by (*ii*),
$$\frac{r_3}{r_2} = \frac{k(1.00)^x\,(1.00)^y}{k(0.50)^x\,(1.00)^y} = \frac{3.2 \times 10^{-4}}{3.2 \times 10^{-4}}$$

or
$$\left(\frac{1.00}{0.50}\right)^x = 1 \quad \text{or} \quad 2^x = 1 \quad \text{or} \quad x = 0$$

∴ Rate law is $\mathbf{r = k[A]^0\,[B_2]^1}$.

Example 6.9. *For the thermal decomposition of acetaldehyde*
$$CH_3CHO(g) \longrightarrow CH_4(g) + CO(g),$$
the following rate data are obtained.

Experiment	*Initial pressure (torr.)*	*Initial rate of increase in total pressure (torr.)*
1	*300*	*0.61 (r_1)*
2	*200*	*0.27 (r_2)*

Predict the order of the reaction.

Solution. For the given reaction,
$$\text{Rate} = k\,[CH_3CHO]^n, \text{ where } n = \text{order of reaction}$$
or
$$\log \text{Rate} = \log k + n \log [CH_3CHO]$$

For the two rates given above,
$$\log r_1 = \log k + n \log [CH_3CHO]_1$$
$$\log r_2 = \log k + n \log [CH_3CHO]_2$$
$$\therefore \quad \log \frac{r_1}{r_2} = n \log \frac{[CH_3CHO]_1}{[CH_3CHO]_2}$$

Hence, the order of reaction,
$$n = \frac{\log r_1/r_2}{\log [CH_3CHO]_1/[CH_3CHO]_2}$$
$$= \frac{\log (0.61/0.27)}{\log (300/200)} = \frac{\log 2.26}{\log 1.50} = \frac{0.354}{0.176} = \mathbf{2.0.}$$

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REVIEW PROBLEMS

6.15. Consider the reaction, $2NO + Cl_2 \longrightarrow 2NOCl$, and the following experimental data. Write the most probable rate equation for the reaction.

Experiment	*[NO]* (*in mol L^{-1}*)	*[Cl_2]* (*in mol L^{-1}*)	*Rate, (mol L^{-1} s^{-1})*
1	0.380	0.380	5.0×10^{-3}
2	0.760	0.760	4.0×10^{-2}
3	0.380	0.760	1.0×10^{-2}

6.16. The rate data obtained for a hypothetical reaction,

$$A + B \longrightarrow 2C \text{ is}$$

[A] (*mol L^{-1}*)	*[B]* (*mol L^{-1}*)	$\frac{d[C]}{dt}$ (*mol L^{-1} min^{-1}*)
1.0	1.0	3.0×10^{-2}
1.5	1.0	4.5×10^{-2}
1.5	0.816	3.0×10^{-2}

Based on above data derive the rate law expression and also calculate the value of rate constant *k*.

6.17. Three experimental runs were carried out for the reaction between Cl_2 and NO.

$$Cl_2(g) + 2\,NO(g) \longrightarrow 2\,NOCl(g)$$

The following rate data were obtained :

Run	*Initial Concentration* *[Cl_2]*	(*mol L^{-1}*) *[NO]*	*Initial Rate* (*mol L^{-1} s^{-1}*)
1	0.020	0.010	2.40×10^{-4}
2	0.020	0.030	2.16×10^{-3}
3	0.040	0.030	4.32×10^{-3}

Determine (*i*) the orders with respect to Cl_2 and NO, (*ii*) the rate law and (*iii*) the rate constant.

6.18. The following rate data were obtained at 303 K for the following reaction :

$$2A + B \longrightarrow C + D$$

Experiment	*[A]* *mol L^{-1}*	*[B]* *mol L^{-1}*	*Initial rate of formation of D*
I	0.1	0.1	6.0×10^{-3} mol L^{-1} min^{-1}
II	0.3	0.2	7.2×10^{-2} mol L^{-1} min^{-1}
III.	0.3	0.4	2.88×10^{-1} mol L^{-1} min^{-1}
IV	0.4	0.1	2.4×10^{-2} mol L^{-1} min^{-1}

What is the rate law ? What is the order with respect to each reactant and the overall order ? What are the units of the rate constant ?

6.19. For the following reaction : $2A + B + C \longrightarrow A_2B + C$

the rate law has been determined to be

$$\text{rate} = k[A]\,[B]^2 \text{ with } k = 2.0 \times 10^{-6}\ \text{mol}^{-2}\ \text{L}^2\ \text{s}^{-1}.$$

For this reaction determine the initial rate of the reaction with [A] = 0.2 mol L^{-1} ; [B] = 0.1 mol L^{-1} ; [C] = 0.5 mol L^{-1}. Determine the rate after 0.04 mol L^{-1} of A has reacted. ***(CBSE 1997)***

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3. Integrated rate law method. We have already discussed in section 6.1 that the instantaneous rate of the reaction is given by the differential equation. For example, for a hypothetical reaction

$$A \longrightarrow \text{products}$$

the differential rate equation is given as $-d[A]/dt$. The differential form of the rate law can be transformed to *integrated form of rate law* by the method of calculus. This is done because the integrated form more conveniently helps us to understand the variation of concentration with time.

The integrated equation, thus, derived is used for determining the rate constant, k, of the reaction. Also as the integrated form yields concentration for all times it is helpful in calculating the time in which the reaction is 25% or 50% or 90% complete and *vice versa*.

Let us illustrate this method by applying it to a first order reaction

$$A \longrightarrow B$$

If the concentration of A is [A] and k is the rate constant, then the differential form of this first order reaction will be

$$\frac{-d[A]}{dt} = k[A]$$

Rearranging the equation, we get

$$\frac{-d[A]}{[A]} = kdt \qquad ...(6.2)$$

On integrating the above equation,

$$\int \frac{-d[A]}{[A]} = \int k\,dt$$

We get,

$$-\ln [A] = k\,t + \text{constant} \qquad ...(6.3)$$

$$\left[\text{Integral of } \frac{d[A]}{[A]} \text{ is } \ln [A]\right]$$

To get the value of constant let us put the value of $t = 0$ in Eqn. (6.3), then

$$-\ln [A]_0 = k \times 0 + \text{constant}$$

or

$$\text{constant} = -\ln [A]_0 \qquad [\because \text{ When } t = 0 \text{ then } [A] = [A]_0 \textit{ i.e.}, \text{ initial conc.}]$$

Substituting this value in Eqn. (6.3), we get

$$-\ln[A] = k\,t - \ln [A]_0$$

or

$$k\,t = \ln [A]_0 - \ln [A]$$

$$k\,t = \ln \frac{[A]_0}{[A]} \qquad ...(6.4)$$

Changing it to common log

$$k\,t = 2.303 \log \frac{[A]_0}{[A]}$$

or

$$\boxed{\mathbf{k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}}} \qquad ...(6.5)$$

Equation (6.5) is the *integrated rate equation* for the first order reaction.

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Equation (6.5) is usually written in another form. Suppose the initial concentration of A is 'a' moles per litre. Suppose, x moles of it get changed to products after time t. Thus, the concentration or reactant A left after time t is (a – x) moles per litre. In such a case

$$[A]_0 = a \text{ and } [A] = (a - x)$$

Hence, equation (6.5) becomes

$$k = \frac{2.303}{t} \log \frac{a}{a-x} \quad ...(6.6)$$

Significance of Integrated Rate Equation

(*i*) If the initial concentration of reactant, $[A]_0$, (or a) and concentration at time t, [A] or $(a - x)$ are known then by putting their values in equation (6.5) [or eqn. (6.6)], the value of k can be calculated.

(*ii*) The integrated rate equation also helps us to evaluate the order of reaction. This is done by substituting the value of $[A]_0$ (or a) and [A] (or $a - x$) in equation (6.5) [or eqn. (6.6)]. If a constant value of k is obtained for different values of t, then the reaction is of first order, otherwise not.

The use of above equation (6.5) or (6.6) in calculation of the order of reaction is illustrated in example 6.9.

(*iii*) The integrated rate equation is also used to evaluate the value of k by graphical method. The equation (6.5) can be written as

$$\frac{kt}{2.303} = \log \frac{[A]_0}{[A]}$$

or

$$\frac{kt}{2.303} = \log [A]_0 - \log [A]$$

or

$$\log [A] = \frac{-k}{2.303} \cdot t + \log [A]_0 \quad ...(6.7)$$

Equation (6.7) can be compared to $y = mx + c$ and represents straight line.

Thus, by plotting a graph of log [A], *i.e.*, log of concentration of the reactant at different intervals of time, against the corresponding time interval, t, we get a straight line as shown in Fig. 6.7. The slope of this straight line is given by :

$$Slope = -\frac{k}{2.303}.$$

From the value of slope, the value of k can be calculated.

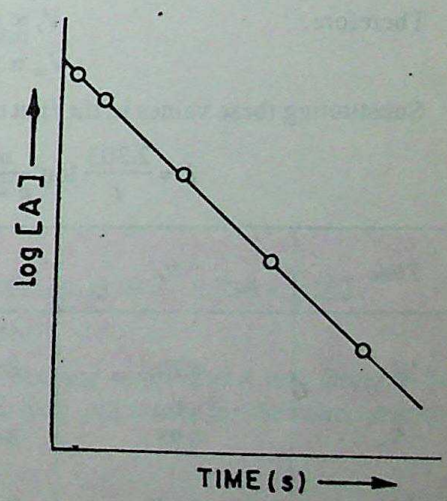

Fig. 6.7

For the sake of convenience, the rate law expressions for the 1st order, 2nd order and 3rd order reactions are given in Table 6.4.

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Table 6.4. Rate Law Expressions for different Reactions

Reaction	*Order*	*Differential form*	*Integrated form*
$A \longrightarrow$ Products	1	rate = $k[A]$	$kt = 2.303 \log \frac{[A]_0}{[A]}$
$2A \longrightarrow$ Products	2	rate = $k[A]^2$	$kt = \frac{1}{[A]} - \frac{1}{[A]_0}$
$A + B \longrightarrow$ Products	2	rate = $k[A][B]$	$kt = \frac{2.303}{[A]_0 - [B]_0} \log \frac{[B]_0[A]}{[A]_0[B]}$
$3A \longrightarrow$ Products	3	rate = $k[A]^3$	$kt = \frac{1}{2}\left[\frac{1}{[A]^2} - \frac{1}{[A]_0^2}\right]$

Example 6.10. *For decomposition of N_2O_5 in CCl_4 solution at 320 K*

$$2N_2O_5 \longrightarrow 4NO_2 + O_2$$

show that the reaction is of first order and also calculate the rate constant :

Time in mts.	:	*10*	*15*	*20*	*25*	∞
Volume of O_2 evolved (in ml.)	:	*6.30*	*8.95*	*11.40*	*13.50*	*34.75*

Solution. If the reaction is of first order, it must obey the equation

$$k = \frac{2.303}{t} \log \frac{a}{(a-x)}$$

In the above reaction, NO_2 remains in solution and oxygen is liberated and collected at different intervals of time.

Therefore,

$$V_t \propto x$$

$$V_\infty \propto a$$

Substituting these values in the first order equation

$$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$$

Time	V_t	$V_\infty - V_t$	$k = \frac{2.303}{t} \log \frac{V_\infty}{V_\infty - V_t}$
10	6.30	34.75 – 6.30 = 28.45	$k = \frac{2.303}{10} \log \frac{34.75}{28.45} = 0.0198$
15	8.95	34.75 – 8.95 = 25.80	$k = \frac{2.303}{15} \log \frac{34.75}{25.80} = 0.0198$
20	11.40	34.75 – 11.40 = 23.35	$k = \frac{2.303}{20} \log \frac{34.75}{23.35} = 0.0198$
25	13.50	34.75 – 13.50 = 21.25	$k = \frac{2.303}{25} \log \frac{34.75}{21.25} = 0.0198$

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Since the value of k comes out to be constant the reaction, therefore, is of first order. The average value of rate constant is **0.0198 min^{-1}**.

Example 6.11. *From the following data, show that the decomposition of hydrogen peroxide is a first order reaction*

Time in minutes	*0*	*10*	*20*
Volume of $KMnO_4$ used in ml.	*46.1*	*29.8*	*19.3.*

Solution. If the reaction is of first order, it would follow the equation

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

In the present case the initial volume, V_0, *i.e.*, volume at $t = 0$ corresponds to initial conc. *i.e.*, a and volume at time t (V_t) corresponds to concentration at time t *i.e.* $a - x$.

Thus, substituting values in above expression the value of k can be calculated

(*i*) at 10 min $\quad k = \frac{2.303}{10} \log \frac{46.1}{29.8} = 0.0436 \text{ min}^{-1}$

(*ii*) at 19.3 min $\quad k = \frac{2.303}{10} \log \frac{46.1}{19.3} = 0.0435 \text{ min}^{-1}$

Since the value of k is nearly same, the reaction is of first order.

Example 6.12. *For the decomposition of N_2O_5 given as*

$$N_2O_5(g) \longrightarrow N_2O_4(g) + \tfrac{1}{2} O_2(g),$$

if the rate law = $k[N_2O_5]$ and $k = 1.68 \times 10^{-2}$ s^{-1}, starting with 2.5 moles of $N_2O_5(g)$ in a 5.0 litre container at 298 K, how many moles of N_2O_5 would remain after 1.0 minute.

Solution. Initial conc. of N_2O_5, $[A]_0$ in mole/litre

$$= \frac{2.5}{5} = 0.5 \text{ mole/litre}$$

According to integrated rate equation for the first order reaction

$$\log \frac{[A]_0}{[A]} = \frac{kt}{2.303}$$

or $$\log \frac{[0.5]}{[A]} = \frac{60 \times 1.68 \times 10^{-2}}{2.303} = 43.76 \times 10^{-2}$$

or $$\log 0.5 - \log [A] = 43.76 \times 10^{-2}$$

or $$\log [A] = \log 0.5 - 43.76 \times 10^{-2} = -0.301 - 0.4376 = -0.738 = \bar{1}.262$$

$$[A] = \text{antilog } \bar{1}.262 = \mathbf{0.182 \text{ mole/litre.}}$$

Example 6.13. *The rate constant for a first order reaction involving compound A was found to be 0.082 min^{-1}. When the initial concentration of A is 0.15 mol/litre, how long will it take for the concentration of A to drop to 0.03 mol/litre.*

Solution. $\quad k = 0.082 \text{ min}^{-1}$

$$k = \frac{2.303}{t} \log \frac{a}{a-x}$$

$$t = \frac{2.303}{0.082} \log \frac{0.15}{0.03} = \frac{2.303}{0.082} \log 5 = \frac{2.303}{0.082} \times 0.6990 = \mathbf{19.6 \text{ min.}}$$

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REVIEW PROBLEMS

6.20. In the oxidation of oxalic acid

when 2 ml of $\left(\begin{matrix}COOH \\ | \\ COOH\end{matrix} \longrightarrow CO + CO_2 + H_2O\right)$

the solution were withdrawn and titrated against standard solution of potassium permanganate, the following results were obtained :

Time in minutes	*Volume of $KMnO_4$ (in ml) required for titration of oxalic acid*
0	22.0
300	17.0
450	15.0
600	13.2

Show that the reaction is of first order.

6.21. Decomposition of ammonium nitrite is a first order reaction,

$$NH_4NO_2 \longrightarrow N_2 + 2H_2O$$

Decomposition of ammonium nitrite was studied at constant temperature. Volume of N_2 collected at different intervals of time was as follows :

Time in minutes :	10	15	20	25	∞
Vol. of N_2 (in ml) :	6.25	9.00	11.4	13.65	35.05

Show that the reaction is of first order.

6.22. In a reaction A → B, the following data were obtained :

t (in sec) :	0	900	1800
Conc. of A :	50.6	19.6	7.62

Show that the reaction is of first order.

6.23. 12.75% of a reaction of first order was completed in 32 minutes. Calculate the rate constant of the reaction.

6.24. A first order reaction is 40% complete in 50 minutes. Calculate the value of rate constant. In what time will the reaction be 80% complete ?

6.25. From the following data show that the decomposition of H_2O_2 in an aqueous solution is a first order reaction where N is the number of ml of $KMnO_4$ required to decompose a definite volume of H_2O_2.

Time (in minutes) :	0	10	20	30
N :	25	16	10.5	7.8

6.26. From the following data for the decomposition of N_2O_5 in CCl_4 at 320 K, show that the reaction is of first order :

Time (in minutes) :	10	15	20	25	∞
V (volume of oxygen) :	6.30	8.95	11.40	13.50	34.74

6.27. Show that the following data conform to the first order reaction :

Time (in minutes) :	0	10	20	30	40
Concentration of reactants in moles per litre :	0.445	0.223	0.112	0.056	0.028

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6.28. In an experiment on the decomposition of an aqueous solution of ammonium nitrite at a certain temperature the volume of nitrogen was collected at different intervals of time as follows :

Time (in seconds)	:	1190	2300	∞
Volume of N_2 (in ml)	:	5.00	7.30	9.50

Show that the data is in agreement with first order reaction.

6.29. For a reaction between potassium and ammonia occurring as $K + NH_3 \longrightarrow K^+ + NH_2^- + \frac{1}{2}H_2$, if the initial concentration of potassium is 1.13×10^{-3} M and concentration after 4 hours and 34 minutes is 8.77×10^{-4} M, calculate the rate constant k. Assume the reaction to be of first order.

6.30. A reaction that is of the first order with respect to reactant A has a rate constant 6.0×10^{-2} min^{-1}. If we start with [A] = 0.5 mol L^{-1}, when would [A] reach the value 0.05 mol L^{-1} ?

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Half Life of a Reaction

It is defined as ***the time during which the concentration of the reactants is reduced to half of the initial concentration or it is the time required for the completion of half of the reaction.*** It is denoted by $t_{1/2}$.

Let us calculate the half life of a first order reaction.

For first order reaction, we know that

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

or

$$t = \frac{2.303}{k} \log \frac{[A]_0}{[A]}$$

when $[A] = \frac{1}{2}[A]_0$, then $t = t_{1/2}$

therefore,

$$t_{1/2} = \frac{2.303}{k} \log \frac{[A]_0}{\frac{1}{2}[A]_0} = \frac{2.303}{k} \log 2$$

$$\boxed{t_{1/2} = \frac{0.693}{k}} \qquad [\because \log 2 = 0.3010]$$

In general, for the reaction of nth order

$$\boxed{t_{1/2} \propto \frac{1}{[A]_0^{n-1}}}$$

Thus, it is quite clear from the above expression that the ***half life period or half change time for first order reaction does not depend upon initial concentration of the reactants. Similarly, the time required to reduce the concentration of the reactant to any fraction of the initial concentration for this type of reactions is also independent of the initial concentration.***

In addition to calculation of $t_{1/2}$, the time required to complete different fractions of a first order reaction can also be calculated.

For example, the time required to complete one-third of the reaction will be given as

$$t_{1/3} = \frac{2.303}{k} \log \frac{a}{a - a/3} = \frac{2.303}{k} \log \frac{3}{2} = \frac{0.406}{k}.$$

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In general, the time required to complete **nth fraction** of a first order reaction is given as follows

$$t_{1/n} = \frac{2.303}{k} \log \frac{[A]_0}{[A]_0 - [A]_0/n} = \frac{2.303}{k} \log \frac{1}{1 - 1/n}.$$

Example 6.14. *The half life period of a reaction of first order is 100 sec. Calculate its rate constant.*

Solution. For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

$\therefore$ $k = \frac{0.693}{t_{1/2}}$

Now, $t_{1/2} = 100$ sec

$\therefore$ $k = \frac{0.693}{100} = \mathbf{6.93 \times 10^{-3}\ sec^{-1}}$.

Example 6.15. *A first order reaction has rate constant of 10^{-2} sec^{-1}. Calculate the half life period for this reaction.*

Solution. For a first order reaction, $t_{1/2} = \frac{0.693}{k}$

$k = 10^{-2}$ sec^{-1}

$t_{1/2} = \frac{0.693}{10^{-2}} = \mathbf{69.3\ sec.}$

Example 6.16. *A first order reaction has $k = 1.5 \times 10^{-6}$ sec^{-1} at 240°C. If the reaction is allowed to run for 10 hours, what percentage of the initial concentration would have changed into products. What is the half life period of this reaction ?* (I.I.T. J.E.E. 1987)

Solution. The first order expression is

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

Let $[A]_0 = 1$ and $[A] = 1 - x$

$k = 1.5 \times 10^{-6}$ sec^{-1} ; $t = 10$ hr

Substituting these values

$$1.5 \times 10^{-6}\ (\text{sec}^{-1}) = \frac{2.303}{10 \times 60 \times 60\ (\text{sec})} \log \frac{1}{1 - x}$$

$$\log \frac{1}{1 - x} = \frac{1.5 \times 10^{-6} \times 36000}{2.303} = 0.0234$$

$$\frac{1}{1 - x} = \text{antilog}\ (0.0234) = 1.055$$

$$1.055 - 1.055x = 1$$

or $$x = \frac{1.055 - 1}{1.055} = \mathbf{0.052.}$$

Thus, 5.2% of initial concentration has changed into products.

Half life period $t_{1/2} = \frac{0.693}{k} = \frac{0.693}{1.5 \times 10^{-6}\ \text{sec}^{-1}} = \mathbf{4.62 \times 10^5\ sec.}$

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REVIEW PROBLEMS

6.31. A first order reaction has a specific reaction rate of 2.31×10^{-3} sec^{-1}. Calculate the half life period of the reaction.

6.32. The half life period for a first order reaction is 100 sec. How long will it take for two-third of the reaction to be completed ?

6.33. Show that the time required for the completion of 3/4th of reaction of first order is twice the time required for completion of 1/2 of the reaction.

6.34. The decomposition of H_2O_2 is a first order reaction. Calculate the half change time and the rate constant for the decomposition from the fact that the fraction decomposed at the end of 50 minutes is 0.75.

6.35. The half change time for the decomposition of N_2O_5 is 5.7 hours and is independent for the initial concentration of N_2O_5. Calculate the specific reaction rate and time required for 90 per cent decomposition.

6.36. Rate constant k for first order reaction has been found to be 5.48×10^{-4} sec^{-1}. Calculate its two-third change time, $t_{2/3}$.

6.37. A certain substance A is mixed with an equal amount of B. At the end of one hour 75% of a A has reacted. How much of A will be left unreacted at the end of 2 hours if the reaction is of first order with respect to A and independent of B ?

6.38. At 874 K the half change period for the decomposition of acetone is 81 seconds and is independent of initial pressure. Calculate the time required for 80% decomposition of acetone.

6.39. A first order reaction is found to have a rate constant $k = 7.39 \times 10^{-5}$ sec^{-1}. Find the half life of this reaction.

6.40. The half life of a first order reaction is 2.50 hours. Calculate the value of the rate constant in sec^{-1}.

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6.5. ENERGY AND ORIENTATION BARRIERS TO REACTIONS—COLLISION THEORY

A number of observed facts of chemical kinetics have been interpreted in the terms of Collision theory. The basic idea of this theory is that a chemical reaction occurs only as a result of collisions between the reacting molecules. During such collisions, atoms get rearranged by breaking up of old bonds and formation of new bonds. Consider for example, the reaction between two diatomic gas molecules X_2 and Y_2 forming two molecules of XY.

$$X_2(g) + Y_2(g) \longrightarrow 2XY(g)$$

The formation of product is possible only if the molecules X_2 and Y_2 collide. For the colliding molecules, *the total number of collisions which occur among the reacting species per second per unit volume is called* **collision frequency.** It is denoted by letter Z*. However, it must be noted here that every collision that occurs between the molecules of X_2 and Y_2 does not result in a reaction. For example, in a gaseous mixture under ordinary conditions of temperature and pressure 10^{25} to 10^{28} binary collision occurs. If all these collisions were effective in bringing about the chemical reaction, the reaction would have been completed in a second or so. But it is not observed in practice. This means that all the collisions in a reaction mixture are not effective in bringing about the chemical reaction. *The collisions which bring about the chemical reaction are called* **effective collisions.**

*According to kinetic theory of gases.

$$Z = \sqrt{2}\, \pi \bar{v} \sigma^2 n^2,$$

where $\bar{v}$ is average velocity, σ = molecular diameter in cm and n = number of molecules per cc.

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There are two important barriers to a reaction, namely, *energy barrier* and *orientation barrier*.

(*i*) **Energy barrier.** For the reacting species to make effective collisions, they must have sufficient energy to cause the breaking of the bonds. We know that the colliding particles are repelled by repulsive forces generated by their electron clouds, therefore the colliding particles should possess sufficient energy that can be utilised to overcome repulsive forces and can cause the atoms in the molecule to vibrate violently. This helps to break the bonds between atoms of reactants. *The minimum amount of energy which the colliding particles must possess in order to bring about chemical reaction is called* **threshold energy.** In a sample of a gas, only a small fraction of molecules have energy equal to or greater than threshold energy. Distribution of energies among molecules in a sample of gas at particular temperature is given by the graph shown in Fig. 6.8. The number of molecules which can have energetically effective collisions is indicated by the shaded area in the graph.

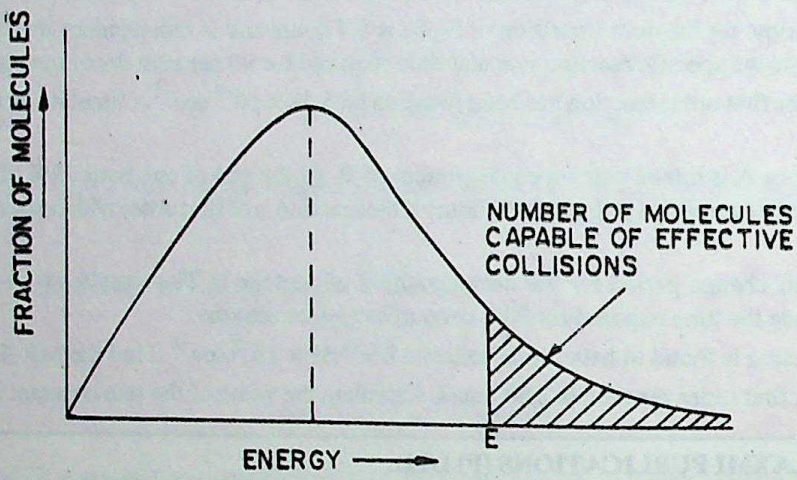

Fig. 6.8. Distribution of energies among the reactant molecules at temperature T.

(*ii*) **Orientation barrier.** It is a well known fact that the damage resulting from collisions of two cars depends on their speed and position of impact. Similarly, in the chemical reactions the colliding species must have proper orientation at the time of collision so that the old bonds break and new bonds are formed.

The collision involving proper orientation has been shown in Fig. 6.9.

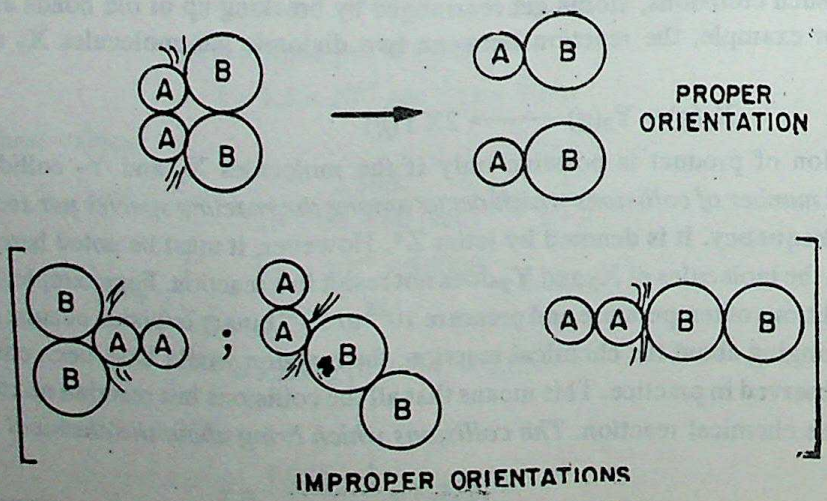

Fig. 6.9

It may be noted that colliding particles having energy less than the threshold energy, even though they are properly oriented, do not produce effective collisions. Similarly, the particles having energy equal to or greater than threshold energy but in proper orientation also bounce back and do not form the products.

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So from collision theory of reaction rates, we conclude that the specific reaction rate (k) is equal to the number of effective collisions per cm^3 per second. Hence, we can write,

$$Rate\ of\ reaction = f \times Z$$

where Z is *collision frequency* and f is the *fraction of collisions which is effective.*

Also, according to kinetic theory of gases the fraction of molecules (f) in a gas possessing energy greater than a particular value of energy (E_a) is given by the equation

$$f = \frac{\Delta n}{N} = e^{-Ea/RT}$$

substituting the value of f in above equation, we get

$$k = Ze^{-E_a/RT}$$

This equation is comparable to Arrhenius equation (section 6.7)

Factors Affecting the Rate of Encounters (Collisions) between Reactant Species.

The rate of encounters between the reacting species depends upon the following factors :

(*i*) **Concentration of the reactions.** Greater is the concentration of reactants, more will be the chances of collisions between the reacting particles, consequently, larger is the rate of the reaction. For gaseous reactants as the concentration is related to the pressure, therefore, greater is the pressure more will be number of molecules per unit volume and consequently, greater will be the rate of encounters between the molecules.

(*ii*) **Surface area.** This factor is more significant in heterogeneous reactions. Larger the surface area of the reacting substances more will be the probability of reacting species coming in contact with each other and, therefore, more will be the number of encounters between them. For example, combustion of a piece of coal in air is relatively slower, whereas combustion of coal dust in air is much faster. Similarly, dissolution of sugar crystals in water is slower but dissolution of powdered sugar is rapid. Thus, we find that the rate of the process is increased if the particle size of the solid state is decreased. In fact, decrease in the particle size increases the surface area. For the sake of comparison, let us consider a cube of dimensions (4 cm × 4 cm × 4 cm).

Total surface area $= 4 \times 4 \times 6$ faces $= 96\ cm^2$

Total volume $= 4 \times 4 \times 4 = 64\ cm^3$

Now if the same cube is divided into 64 cubes each having dimensions (1 cm × 1 cm × 1 cm), then

Surface area of 64 cubes $= 64 \times 6 = 384\ cm^2$

Total volume of 64 cubes $= 1\ cm^3 \times 64 = 64\ cm^3$.

The above example proves that dividing the solid particles into smaller size results in the increase of surface area. This enhances the chances of encounters and thus, makes the reaction faster.

6.6. EFFECT OF TEMPERATURE ON REACTION RATE

The rates of almost all reactions increase with the increase in temperature. In most of the cases the rate of the reaction becomes almost double for every 10° rise of temperature. This is also expressed in the terms of **temperature coefficient** which is the ratio of rate constants of the reaction at two temperatures differing by 10°. The two temperatures generally selected are 298 K and 308 K. Thus,

$$Temperature\ coefficient = \frac{Rate\ constant\ of\ 308\ K}{Rate\ constant\ at\ 298\ K}.$$

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The rate constants for the decomposition of N_2O_5 at different temperatures is given in Table 6.5. From the table, it is seen that rate constant at 273 K is 7.87×10^{-7} and at 298 K is 3.56×10^{-5}. This shows that for 25° rise of temperature of the rate constant increases by 43 times.

Table 6.5. Rate constants for the decomposition of N_2O_5 at different temperatures

Temperature (K)	*k (sec^{-1})*
273	7.87×10^{-7}
298	3.56×10^{-5}
308	13.5×10^{-5}
318	4.98×10^{-4}
328	15.0×10^{-4}
338	4.87×10^{-3}

Explanation of the Effect of Temperature

According to collision theory of reaction rates, → frac. of total no. of effective collisions

Rate of a reaction = $f \times Z$ → collision freq.

Thus, the increase in rate is due to either of the above factors *i.e.*, f or Z or due to both of these.

It may be seen that the increase in the total number of collisions per unit volume per unit time (collision frequency) is not so much responsible for the higher reaction rate as is the increase in the fraction of effective collisions. Let us, for example, calculate the increase in collision frequency when temperature increases from 298 to 308 K. As we knows that the collision frequency is directly proportional to the square root of absolute temperature, therefore, the ratio of collision frequencies at these temperatures follows as,

$$\frac{Z_{308}}{Z_{298}} = \sqrt{\frac{308}{298}} = 1.016.$$

From the above ratio it is clear that there is a insignificant increase in the collision frequency. Hence, it cannot explain the observed increase in the rate of the reaction with increase in temperature.

Let us now consider the effect of increase in temperature on the number of effective collisions.

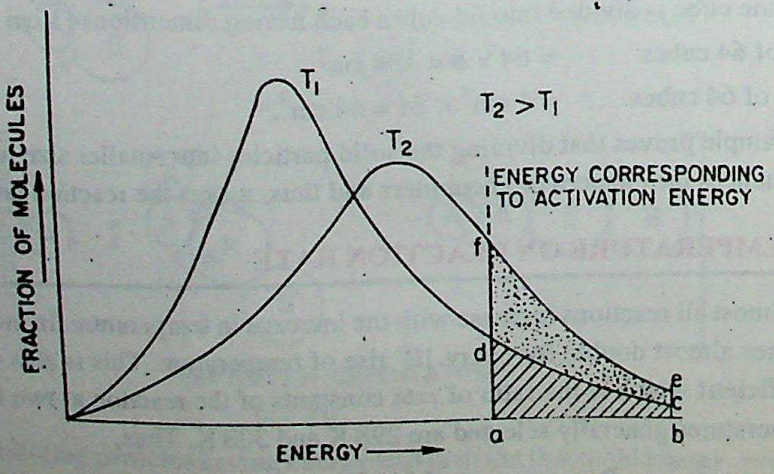

Fig. 6.10. Energy distribution at different temperatures.

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On the basis of probability consideration Fig. 6.10 is drawn to give the energy distribution curves at temperatures T_1 and T_2 (where $T_2 = T_1 + 10$). Now as we know that the rise in temperature increases the kinetic energy of molecules ($\because$ K.E. $\propto$ T) therefore, the energy distribution curve gets flattened and shifts towards higher energy region. A close examination of the curves in the graph clearly reveals that the function of molecules possessing higher kinetic energy, *i.e.*, energy greater than threshold energy, as indicated by shaded portion becomes almost double and therefore *the rate of reaction almost doubles for 10° rise of temperature.* Thus, increase in the rate of reaction with increase in temperature is mainly due to increase in number of collisions which are energetically effective.

6.7. CONCEPT OF ACTIVATION ENERGY

For a reaction to take place molecules of reactants must collide with each other. Out of the total number of collisions only those collisions result in the formation of products which possess energy equal to or more than the certain minimum energy called threshold energy. Collisions of the molecules possessing energy less than threshold energy do not form products. It means that between reactants and products there is an energy barrier which must be crossed before the reactants are converted into products. The energy required for crossing this energy barrier is supplied by the kinetic energy of the molecules.

***"The minimum extra energy over and above the average potential energy of the reactants which must be supplied to the reactants to enable them to cross over the energy barrier between reactants and products is called* Activation energy"**. In other words,

Activation Energy =

(Threshold Energy) – (Average energy of the reactants)

or $E_a = E_T - E_R$

The idea of activation energy and the energy barrier involved in a reaction is represented graphically in Fig. 6.11.

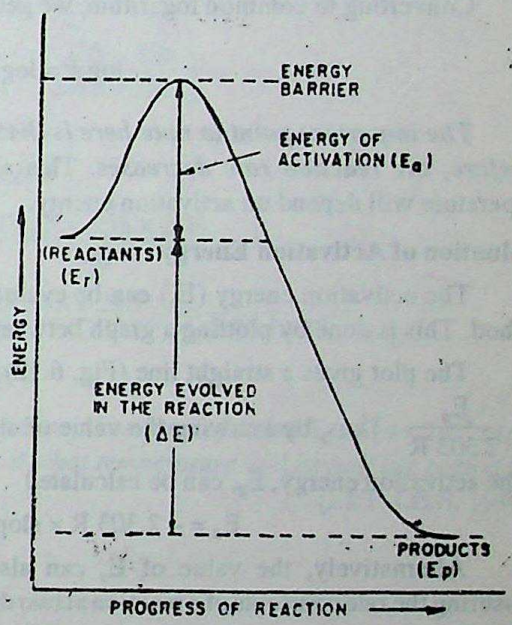

Fig. 6.11. Illustration of activation energy and energy barrier involved in a rection.

Each reaction has a definite value of E_a and this decides the fraction of total collisions which are effective. Obviously, if the activation energy for a reaction is low, large number of molecules can have this energy and the fraction of effective collision, *f*, will be large. Such a reaction proceeds at high rate. On the other hand, if the activation energy is high, then *f* will be small and the reaction may be quite slow.

In short,

For fast reactions ; *activation energies are low.*

For slow reactions ; *activation energies are high.*

For example, for the reaction between NO and O_2, E_a is low and hence, reaction is fast whereas for the reaction between CO and O_2, E_a is high and hence, the reaction is slow.

$$2NO + O_2 \longrightarrow 2NO_2 \quad (Fast)$$

$$2CO + O_2 \longrightarrow 2CO_2 \quad (Slow)$$

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Arrhenius Equation

Arrhenius developed the mathematical relation between *temperature* and the *rate constant* on the basis of the observations from the large number of experiments. This temperature dependence of the rate constants is expressed algebraically as,

$$k = Ae^{-E_a/RT} \quad ...(6.8)$$

Equation (6.8) is called *Arrhenius equation.* Here A is pre-exponential factor and is called *frequency factor,* E_a is the *energy of activation* and T is the temperature in kelvin scale. Both A and E_a are characteristic of the reaction. Another form of the equation which is more useful for calculations is obtained by taking logarithm of Eqn. (6.8), therefore,

$$\ln k = \ln A - \frac{E_a}{RT} \quad [\because \ln e = 1]$$

Converting to common logarithm, we get

$$\log k = \log A - \frac{E_a}{2.303\,R}\frac{1}{T} \quad ...(6.9)$$

The important point to note here is that as the value of E_a increases, the value of k decreases and therefore, the reaction rate decreases. This also means that the magnitude of this effect of increasing temperature will depend on activation energy.

Evaluation of Activation Energy

The activation energy (E_a) can be evaluated by the graphical method. This is done by plotting a graph between log k against 1/T.

The plot gives a straight line (Fig. 6.12) having a slope equal to $-\frac{E_a}{2.303\,R}$. Thus, by knowing the value of slope and gas constant R, the activation energy, E_a, can be calculated

$$E_a = -2.303\,R \times \text{slope}$$

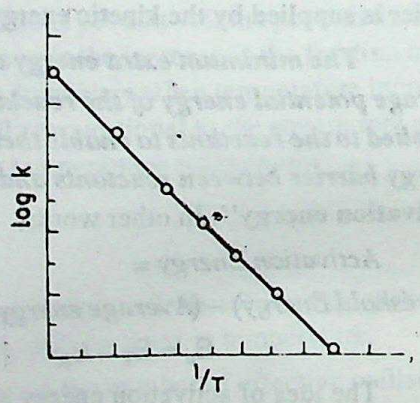

Fig. 6.12. Plot of log k vs 1/T.

Alternatively, the value of E_a can also be determined by measuring the rate constants of a reaction at two different temperatures. If k_1 and k_2 are the rate constants for the reaction at temperatures of T_1 and T_2, then

$$\log k_1 = \log A - \frac{E_a}{2.303\,RT_1} \quad ...(6.10)$$

$$\log k_2 = \log A - \frac{E_a}{2.303\,RT_2} \quad ...(6.11)$$

Subtracting Eq. (6.10) from Eq. (6.11), we get

$$\log k_2 - \log k_1 = \frac{E_a}{2.303\,R}\left[\frac{1}{T_1} - \frac{1}{T_2}\right]$$

or

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right] \quad ...(6.12)$$

Let us now see that how the rate constant of a reaction varies when the temperature is increased by 10° from 300 to 310 K. In general, for many of the reactions the activation energy (E_a) is about 55 kJ mol^{-1} near room temperature. Hence,

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$$\log \frac{k_2}{k_1} = \frac{55{,}000}{2.303 \times 8.314}\left(\frac{310 - 300}{300 \times 310}\right) = 0.30887$$

or
$$\frac{k_2}{k_1} = \text{antilog } 0.30887 = 2.03 \simeq 2.0$$

Thus, it is quite clear that for majority of reactions the rate constant doubles for 10° rise in temperature near room temperature.

Example 6.17. *The value of rate constant for the decomposition of nitrogen pentoxide,* $N_2O_5 \longrightarrow N_2O_4 + \frac{1}{2}O_2$, *is* 3.46×10^{-5} *at 25°C and* 4.87×10^{-3} *at 65°C. Calculate the energy of activation for the reaction* ($R = 8.314\ JK^{-1}\ mol^{-1}$).

Solution. We know that
$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

$$\log \frac{4.87 \times 10^{-3}}{3.46 \times 10^{-5}} = \frac{E_a}{2.303 \times 8.314} \times \left(\frac{338 - 298}{338 \times 298}\right)$$

$$\log 140.75 = \frac{E_a}{19.15}\left[\frac{40}{338 \times 298}\right]$$

$$E_a = \log 140.75 \times \frac{19.15 \times 338 \times 298}{40}$$

$$= \frac{2.148 \times 19.15 \times 338 \times 298}{40} = 103584\ \text{J mol}^{-1}$$

$$= \mathbf{103.58\ kJ\ mol^{-1}}.$$

Example 6.18. *In the Arrhenius equation for certain reaction, the values of A and* E_a *are* $4 \times 10^{13}\ sec^{-1}$ *and 98.6 kJ* mol^{-1} *respectively. If the reaction is of first order at what temperature will its half life period be 10 min.* (I.I.T. J.E.E. 1990)

Solution. The Arrhenius equation is
$$k = A\, e^{-E_a/RT}$$

Taking logarithm of both sides,
$$\ln k = \ln A - E_a/RT$$

or
$$\ln \frac{k}{A} = -E_a/RT$$

or
$$\log \frac{k}{A} = -\frac{E_a}{2.303\ RT} \quad ...(1)$$

Now,
$$k = \frac{0.693}{t_{1/2}} = \frac{0.963}{10 \times 60\ \text{sec}} = 1.155 \times 10^{-3}\ \text{sec}^{-1}$$

Substitute the values in equation (1)
$$\log \frac{1.155 \times 10^{-3}\ \text{sec}^{-1}}{4 \times 10^{13}\ \text{sec}^{-1}} = \frac{-98.6 \times 10^3\ \text{J mol}^{-1}}{8.314 \times T \times 2.303}$$

$$-16.54 = \frac{-98600}{19.147\ T}$$

or
$$T = \frac{98600}{19.147 \times 16.54} = \mathbf{311.34\ K.}$$

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REVIEW PROBLEMS

6.41. Calculate the activation energy of a reaction whose rate constant is tripled by a 10° rise is temperature, in the vicinity of 27°C.

6.42. The rate constant of a second order reaction is 5.70×10^{-5} mol^{-1} L s^{-1} at 25°C and 1.64×10^{-4} mol^{-1} L s^{-1} at 40°C. Calculate the activation energy and the Arrhenius frequency factor, A.

6.43. The rate constant k, for the first order gas phase decomposition of ethyl iodide, $C_2H_5I \longrightarrow C_2H_4 + HI$ is 1.60×10^3 s^{-1} at 600 K and 66.3×10^5 s^{-1} at 700 K. Calculate E_a of the reaction.

6.44. Calculate the activation energy for a reaction which doubles in rate when the temperature is raised from 18° C to 28°C.

6.45. The rate of a particular reaction doubles when temperature changes from 27°C to 37°C. Calculate the energy of activation for such a reaction (R = 8.314 JK^{-1} mol^{-1}). *(A.I. CBSE 1992)*

6.46. The rate of a particular reaction quadruples when the temperature changes from 293 K to 313 K. Calculate the energy of activation for such a reaction.

6.47. The rate constant for the decomposition of N_2O_5 at various temperatures are as follows :

T°(C)	0	25	35	45	55	65
k(s^{-1})	7.9×10^{-7}	3.5×10^{-5}	1.35×10^{-4}	5.0×10^{-4}	1.5×10^{-3}	4.9×10^{-3}

Draw a graph and from it determine the activation energy of the reaction.

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Activated Complex or Transition State

It has been pointed out earlier that during the chemical reaction certain bonds are broken and certain new bonds are formed. The breaking of bonds requires energy whereas the formation of bonds results in the release of energy. For example, in the reaction of hydrogen with iodine to form hydrogen iodine, when a

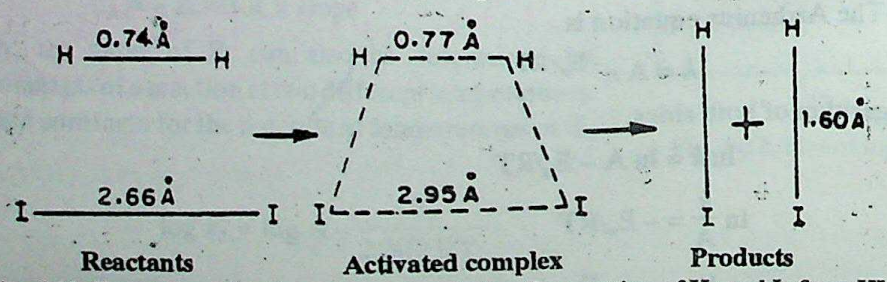

Fig. 6.13. Formation of activated complex during the reaction of H_2 and I_2 from HI.

molecule of hydrogen approaches that of iodine, H—H and I—I bonds start breaking and H—I bonds start forming. In the beginning, breaking of bonds predominates and therefore, energy of the system starts increasing till it reaches a maxima (corresponding to threshold energy). After this, the energy starts decreasing because the process of bond formation predominates and finally leads to the product hydrogen iodide. ***The arrangement of atoms corresponding to energy maxima (threshold energy)*** is called **transition state or activated complex.** In transition state, the system has partial reactant character and partial product character as shown in Fig. 6.13 and Fig. 6.14.

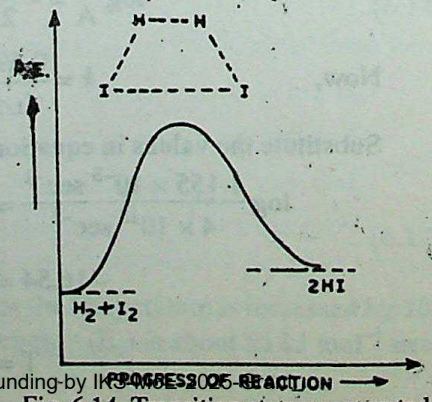

Fig. 6.14. Transition state or activated complex.

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The difference between energy of the transition state and energy of the reactants is equal to activation energy.

$$E_{transition\ state} - E_{reactants} = E_{activation}$$

Kinetic Stability of Fuels

The unusual stability of fuels even in the presence of oxygen or air can now be explained on the basis of concept of activation energy. In general, the activation energy of combustion reactions is quite high. When a flame is applied to the mixture of fuel and air, the contents near the flame are raised to high temperature. The supplied energy is enough to cause the combustion of a portion of fuel in oxygen. The heat liberated by the combustion increases the temperature of remaining fuel and the flame once produced is sustained. Thus, we realise that many reactions which are feasible from the consideration of free energy may be prevented from occurring due to high activation energy barrier. Such energy barriers are blissful for the existence of life on earth because they provide stability to the reactants like fuels, contents of explosives in bombs, etc., which otherwise are unstable from the point of view of thermodynamics. This leads us to make a concluding statement that ***the reactants which are thermodynamically unstable at ordinary temperature may not be kinetically unstable.***

6.8. PHOTOCHEMICAL REACTIONS

There are many chemical reactions whose rates are influenced by radiations, particularly *ultra violet* and *visible light.* Such reactions are called **photochemical reactions.** Some common examples of such reactions are *photosynthesis, photography, blue printing, photochemical synthesis of compounds*, etc.

Some **important observations** of photochemical reactions are :

(*i*) Photochemical reactions do not occur in dark.

(*ii*) Different reactions use different frequencies of radiations for their initiation. For example, the reactions which require the photons of voilet radiation (more energetic) for their occurrence may not be initiated by the photons of yellow light.

(*iii*) The ΔG value of the photochemical reaction may or may not be negative.

(*iv*) At low intensities, the rates of photochemical reactions depend upon the intensity of radiation, instead of the concentrations of reactants.

(*v*) Temperature does not have marked effect on the rates of photochemical reactions.

Role of light in photochemical reactions

In photochemical reactions, the photons of radiant energy ($h\nu$) are absorbed by the molecules of reacting substances. The absorbed energy in such cases is sufficient enough to activate the reactants to cross the energy barrier existing between reactants and products. In other words, the radiant energy initiates the chemical reaction by supplying necessary activation energy required for the reaction.

Mechanism of photochemical reaction

Let us understand the mechanism of a simple photochemical process, the **photosynthesis of hydrogen chloride** as described below.

$$H_2 + Cl_2 \xrightarrow{light} 2HCl$$

The above reaction occurs violently when the mixture of H_2 and Cl_2 is exposed to sunlight. Here, sunlight provides sufficient energy to cause dissociation of chlorine molecules into atoms.

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In fact, Cl_2 molecule *absorbs photon of energy, get excited* and dissociates into highly energetic chlorine atoms.

$$Cl_2 + h\nu \longrightarrow \underset{\text{Excited molecule}}{Cl_2^*} \longrightarrow \underset{\text{Chlorine atoms}}{Cl + Cl} \quad ...(1)$$

One Cl atom then combines with hydrogen molecule, H_2 to form HCl molecule and H atom. The highly reactive H atom further combines with Cl_2 molecule to produce HCl molecule and Cl atom as shown below :

$$Cl + H_2 \longrightarrow HCl + H \quad ...(2)$$

$$H + Cl_2 \longrightarrow HCl + Cl \quad ...(3)$$

It is evident that in step 3, there is a regeneration of reactive chlorine atom again. In fact, steps (2) and (3) are repeated again and again. Such sequence of steps constitutes a **chain reaction process.** It can be realised that the concentration of chlorine atoms build up very rapidly, once they are initially formed in step (1). This quick build up of reactive species can lead to explosive situation in this case. The chain process continues till almost whole of the reactants are consumed. The reaction stops when Cl atoms left off combine with each other to form Cl_2 molecules.

$$Cl + Cl \longrightarrow Cl_2 \quad ...(4)$$

Destruction of ozone layer

Formation and dissociation of ozone in the stratosphere (≈ 11 – 50 km from the surface of earth) can be represented as

$$O_2 \xrightarrow{h\nu} O + O$$

$$O + O_2 \longrightarrow O_3$$

$$O_3 \xrightarrow{h\nu} O_2 + O + \text{heat}$$

The formation and dissociation of ozone keep the ozone-oxygen balance in ozone layer. However chlorofluoromethanes like $CFCl_3$ and CF_2Cl_2 (Freon) which are used as aerosol propellants and in refrigerators, have diffused into ozone layer and disturbed the natural ozone balance. A possible mechanism involved is as follows :

A photon of sunlight of sufficient energy causes the breaking up of the chlorine atom from a molecule of CF_2Cl_2.

$$CF_2Cl_2 + h\nu \longrightarrow CF_2Cl + Cl \quad ...(1)$$

The chlorine atom being highly energetic starts a chain of reactions by reacting with ozone and forming chlorine monoxide.

$$Cl + O_3 \longrightarrow ClO + O_2 \quad ...(2)$$

The monoxide obtained again reacts with O_3 to generate chlorine atoms which are used again in step 2.

$$ClO + O_3 \longrightarrow Cl + 2O_2 \quad ...(3)$$

So, in this way steps 2 and 3 are repeated again and again to cause the destruction of ozone layer.

Difference between Photochemical and Thermochemical Reactions. Some significant differences between photochemical and thermochemical reactions are given below in tabular form :

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Photochemical reactions	*Thermochemical reactions*
1. These reactions are initiated by light radiations.	1. These reactions are initiated by heat energy.
2. They cannot occur in dark.	2. They can occur in dark.
3. Temperature does not have any significant effect on the rates of such reactions.	3. The temperature has a marked effect on the rates of these reactions.
4. Temperature coefficient is low.	4. Temperature coefficient is generally high.
5. The value of ΔG may be + ve or – ve.	5. ΔG is – ve for such reactions.

Photosensitization

There are many substances which do not react directly when exposed to light. However, if another substance is added, the photochemical reaction starts. The substance, thus, added itself does not undergo any chemical change. It merely absorbs the light energy and then passes it on to one of the reactants. *Such a substance which when added to the reaction mixture helps to start the photochemical reaction but itself does not undergo any chemical change* is called **a photosensitizer** and the process is called **photosensitization.** Thus, a photosensitizer simply acts as a *carrier of energy.*

A common example of photosensitization is *photosynethesis of carbohydrates in plants.* This is process occurring in plants everyday during the sunlight. Carbon dioxide and water vapour present in the air do not absorb the visible light (emitted by the sun). However, the green colouring matter, *chlorophyll* present in the plants can absorb the visible light. After absorption, it passes on the energy to carbon dioxide and water molecules which then combine after undergoing a series of reactions to ultimately form carbohydrates alongwith the evolution of oxygen.

Another common example involving photosensitisation reaction is the combination of H_2 and CO to give a HCHO and OHC—CHO (glyoxal) as the products. Here Hg (mercury) vapours (when irradiated to a light of 254 nm wavelength) serve as a photosensitizer to initiate the reaction between H_2 and CO. The mercury vapour brings about the dissociation of hydrogen molecule into energetic H atoms which then brings about the following sequence of reactions :

$$Hg + h\nu \longrightarrow Hg^* \quad ...(1)$$

$$Hg^* + H_2 \longrightarrow 2H + Hg \quad ...(2)$$

$$H + CO \longrightarrow HCO \quad ...(3)$$

$$HCO + H_2 \longrightarrow HCHO + H \quad ...(4)$$

$$2HCO \longrightarrow HCHO + CO \quad ...(5)$$

$$2HCO \longrightarrow CHO—CHO \text{ (glyoxal)} \quad ...(6)$$

Importance of Photochemical Reactions

Photochemical reactions play significant role in our daily life. Some of the phenomena which are based on photochemical changes are :

(*i*) Photosynthesis in plants

(*ii*) Vision.

(*iii*) Photography.

(*iv*) Photoetching in electronic industry

(*v*) Some polymerisation reactions.

(*vi*) Modern printing technology.

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Damaging effect of photochemical reactions. The common damaging effect of photochemical change that we come across is the effect of sun light on the dyes used in colouring the fabric and other materials. The dyes undergo some photochemical changes in sun light due to which they lose their colour. This causes fading away of coloured fabrics.

6.9. STUDY OF FAST REACTIONS

It has been pointed out in the begining of this chapter that rates of chemical reactions differ from very slow to very fast. Some of the instaneous reactions are so fast that they occur in 10^{-2} seconds (*1 pico second*) or even less time.

Some examples are

(*i*) *Combination of H^+ and OH^- ions during neutralisation of acid-base*

$$H^+(aq) + OH^-(aq) \longrightarrow H_2O(l) \; ; \qquad (t_{1/2} \approx 10^{-10}\ s)$$

(*ii*) *Photosynethesis in plants*

$$6CO_2 + 6H_2O \xrightarrow{\text{Light}} C_6H_{12}O_6 + 6O_2 \; ; (t_{1/2} \approx 10^{-12}\ s)$$

(*iii*) *Isomerisation of retinal in vision* ; $(t_{1/2} \approx 10^{-12}\ s)$

Rates of fast reactions

Rates of fast reactions cannot be measured by the ordinary method, which we have discussed in previous sections, because of the difficulty in measuring the concentration changes in such a short span of time. However, in recent years new experimental techniques have been developed to measure the rates of fast reaction. The various techniques are ***flow methods, relaxation methods*** and ***spectrophotometric techniques.*** The details of these methods is beyond the scope of this book.

Let us study some examples of fast reactions

(*i*) **Photosynthesis in plants.** This is a fast reaction in which CO_2 and H_2O are converted into carbohydrates by green pigment, chlorophyll of the plant in the presence of sun light. The reaction was studied by ***flash-photolysis*** technique. The reaction occurs in the **following steps** :

In the first step, the chlorophyll molecule absorbs a photon of red light and gets excited. Within a few pico-seconds of the absorption of light, it loses its excess energy by undergoing a chemical reaction in which it transfers an electron to a nearby molecule called electron acceptor (A).

The electron acceptor (A) transfers this electron to another molecule (B) which is another electron acceptor. During these steps (*ii*) and (*iii*), energy is released which is used for the synthesis of energy rich molecules from carbon dioxide of the atmosphere. After going through a series of reactions (fast and slow) glucose is produced as the final product. These steps are :

$$Chl \xrightarrow{\text{photon}} Chl^*$$
(Excited molecule)

$$Chl^* + A \longrightarrow Chl^* + A^-$$
(Occurs in a few pico seconds)

$$A^- + B \longrightarrow A + B^-$$
(After 150 pico seconds)

$$B^- + C \longrightarrow B + C^- + \text{Energy}$$

After several steps, the final reaction is

$$6CO_2 + 6H_2O \longrightarrow C_6H_{12}O_6 + 6O_2$$

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The synthesis of sugar takes place at one site of the plant cell and oxidation of water into oxygen at some another site where chlorophyll molecule provides the necessary energy by absorbing a photon of red light.

(*ii*) **Phenomenon of vision.** It involves two steps :

(*a*) The molecule of *retinal* (a light sensitive compound present in the retina of the eye).

As a result, it gets excited and undergoes geometrical isomerisation and the energy absorbed is stored as chemical energy. This step takes only a few picosconds ($\approx 10^{-12}$ s).

(*b*) Within a very short time after the first step, retinal is converted back into its original form and the energy released is used to send a signal to the brain. Hence we have the sensation of vision.

SOME MISCELLANEOUS PROBLEMS

Example 6.19. *What percentage of the initial concentration of reactant reacts in 2.0 hours for a reaction whose rate constant is 4.25×10^{-5} sec^{-1} ?*

Solution. Let the initial conc. of the reactant,

$$[A]_0 = 100 \text{ mol/litre}$$

Say, the conc. that reacts in 2.0 hours = x mol/litre

$\therefore$ Concentration of reactant left after 2.0 hours = $(100 - x)$ mol/litre

$$\text{Rate constant, } k = 4.25 \times 10^{-5} \text{ sec}^{-1}$$

$$\text{Time, } t = 2.0 \times 60 \times 60 = 7200 \text{ sec.}$$

According to first order integrated equation,

$$\log \frac{[A]_0}{[A]} = \frac{kt}{2.303} = \frac{4.25 \times 10^{-5} \times 7200}{2.303} = 13287 \times 10^{-5} = 0.1328$$

Hence,
$$\frac{[A]_0}{[A]} = \text{Antilog } 0.1328 = 1.358$$

or
$$\frac{100}{100 - x} = 1.358$$

$$100 - x = \frac{100}{1.358}$$

$$100 - x = 73.64$$

$$x = 100 - 73.64 = \mathbf{26.36\%}.$$

Example 6.20. *A first order reaction is 20% complete in 10 minutes. Calculate (i) k of the reaction and (ii) time taken for the reaction to go upto 75% completion.*

Solution. Let initial conc. of the reactant,

$$[A]_0 = 100 \text{ mol/litre}$$

Say, the percentage of reactant that reacts in 10 minutes = x mol/litre = 20 mol/litre

Conc. of reactant after 10 minutes = (100 – 20) mol/litre

According to integrated equation for a first order reaction

$$k = \frac{2.303}{t} \log \frac{[A]_0}{[A]} = \frac{2.303}{10} \log \frac{100}{100 - 20}$$

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$$= \frac{2.303}{10}(\log 10 - \log 8) = 0.2303 \times (1 - 0.9031) = 0.2303 \times 0.0969$$

$$= 0.02231 \text{ min}^{-1}.$$

(*ii*) Let the time for 75% completion = t minutes

∴ Percentage of reactant that reacts in time t,

$$x = 75 \text{ mol/litre}$$

The percentage left after time, t = 100 – 75 = 25 mol/litre

Since,
$$t = \frac{2.303}{k}\log\frac{[A]_0}{[A]} = \frac{2.303}{0.02231}\log\frac{100}{25}$$

$$= \frac{2.303}{0.02231}\log 4 = \frac{2.303}{0.02231} \times 0.6021 = \mathbf{62.15 \text{ min.}}$$

Example 6.21. *The rate of reaction triples when the temperature changes from 20° to 50°C. Calculate the energy of activation ($R = 8.314\ JK^{-1}\ mol^{-1}$).* (A.I. CBSE 1991)

Solution. We know that

$$\log\frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

Here,
$$\frac{k_2}{k_1} = 3\ ;\ T_1 = 20 + 273 = 293 \text{ K}$$

$$T_2 = 50 + 273 = 323 \text{ K}$$

$$R = 8.314 \text{ JK}^{-1} \text{ mol}^{-1}$$

Substituting the values
$$\log 3 = \frac{E_a}{2.303 \times 8.314}\left(\frac{323 - 293}{323 \times 293}\right)$$

$$0.4771 = \frac{E_a}{19.147} \times \frac{30}{94639}$$

$$E_a = \frac{0.4771 \times 19.147 \times 94639}{30}$$

$$= 28817.9 \text{ J mol}^{-1} = \mathbf{28.8\ kJ\ mol^{-1}}.$$

Example 6.22. *The following rate data was obtained for the first order thermal decomposition of $SO_2Cl_2(g)$ at a constant volume.*

$$SO_2Cl_2(g) \longrightarrow SO_2(g) + Cl_2(g)$$

Exp.	*Time (sec^{-1})*	*Total pressure (atm)*
1.	*0*	*0.5*
2.	*100*	*0.6*

Calculate the reaction rate when total pressure is 0.65 atmosphere.

Solution. Let us say that the pressure of SO_2Cl_2 decreases by x atm, then the increase of pressure of SO_2 and Cl_2 = x atm each. [∵ 1 mole of SO_2Cl_2 decomposes to give 1 mole of SO_2 and 1 mole of Cl_2]

	$SO_2Cl_2(g)$	⟶	$SO_2(g)$	+	$Cl_2(g)$
Pressure at $t = 0$	0.5 atm		0		0
Pressure at time t,	(0.5 – x atm)		x atm		x atm

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Since total pressure (P_T) $= P_{SO_2Cl_2} + p_{SO_2} + p_{Cl_2}$

$$= (0.5 - x) + x + x$$

$$P_T = 0.5 + x \quad \text{or} \quad x = P_T - 0.5$$

Hence $p_{SO_2Cl_2} = 0.5 - (P_T - 0.5)$

$$= 0.5 - P_T + 0.5 = 1.0 - P_T$$

Since, at t = 100 sec., P_T = 0.6 atm

$\therefore$ $p_{SO_2Cl_2} = 1.0 - 0.6 = 0.4$ atm.

(*a*) Evaluation of k

$$k = \frac{2.303}{t} \log \frac{\text{Initial pressure}}{\text{Pressure at time } t}$$

$$= \frac{2.303}{100} \log \frac{0.5}{0.4} = \frac{2.303}{100} \log 1.25$$

$$= \frac{2.303}{100} \times 0.0969 = \mathbf{2.23 \times 10^{-3}\ sec^{-1}}.$$

(*b*) Rate at P_T = 0.65 atm

$p_{SO_2Cl_2}$ at total pressure of 0.65 atm

$$= 1.0 - 0.65 = 0.35 \text{ atm}$$

$$\text{Rate} = k[N_2O_5] = 2.23 \times 10^{-3} \times 0.35$$

$$= \mathbf{7.8 \times 10^{-4}\ atm\ sec^{-1}}.$$

REVIEW PROBLEMS

6.48. The half life, $t_{1/2}$ for a first order decomposition of NH_4NO_2 is 123 minutes at 15°C.

(*a*) What is the value of k ?

(*b*) How long will it take for 2.0 g of NH_4NO_2 to decompose until 0.20 g remains ?

6.49. If the half-life of a first order reaction ; $A \longrightarrow B$ is 2 min, how long will it take [A] to reach 25 per cent of its initial concentration, 10 per cent of its initial concentration ?

6.50. The thermal decomposition of acetone, CH_3COCH_3 at 600°C is a first order reaction with a half life of 80 s. Calculate (*i*) Rate constant, k, (*ii*) What time will be required for 25 per cent of the given sample to decompose ? (*iii*) Time required for 85% sample to get decomposed.

6.51. For a first order reaction, $A \longrightarrow B + C$, if at the start of the reaction 10 g of A was taken then what is the amount left after (*i*) 3 half lives ? (*ii*) after 6 half lives.

6.52. 60% of a first order reaction was completed in 60 minutes. In what time will 75% of reaction be completed.

6.53. A first order reaction is 20% complete in 10 minutes calculate the time taken for the 80% of reaction to be complete.

[A.I. CBSE (O) 1993]

6.54. The first order thermal decomposition of $N_2O_5(g)$ takes place as follows :

$$2N_2O_5(g) \longrightarrow 2N_2O_4(g) + O_2(g)$$

Time (sec)	:	0	50
Total pressure (atm)	:	0.2	0.25

Calculate the reaction rate when the total pressure is 0.28 atm.

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6.55. The number of flashes of a firefly changes with temperature as follows :

t°C	*Number of flashes per minute*
25	7
28	10
32	20
35	31
38	47
42	82
44	108

Determine the energy of activation for the chemical reaction that leads to the flash.

6.56. The activation energy of a first order reaction at 27°C is 54 kJ mol^{-1}. In the presence of a catalyst the activation energy of the same reaction lowers to 44 kJ mol^{-1} at 27°C. How many times the reaction rate changes in the presence of a catalyst at 27°C ? **Ans.** 55

6.57. The specific rate constant for the reaction of H_2 with I_2 to form HI is 0.43 at 673 K. If the activation energy is 171.5 kJ mol^{-1}, what is the rate constant at 773 K ?

6.58. The experimental data for the decomposition of nitrogen pentoxide in the gaseous phase at 318 K is as follows :

$$2N_2O_5(g) \longrightarrow 4NO_2(g) + O_2(g)$$

Time (seconds)	*$[N_2O_5]$ (mol L^{-1})*
0	1.63×10^{-2}
400	1.36×10^{-2}
800	1.14×10^{-2}
1200	0.93×10^{-2}
1600	0.78×10^{-2}
2000	0.64×10^{-2}
2400	0.53×10^{-2}
2800	0.43×10^{-2}
3200	0.35×10^{-2}
3600	0.29×10^{-2}

(*a*) Plot $[N_2O_5]$ *vs.* time.

(*b*) Find the time taken for the concentration of N_2O_5 to change from 1.63×10^{-2} mol L^{-1} to half the value.

(*c*) Plot $\log_{10} [N_2O_5]$ *vs.* time

(*d*) What is the rate law ?

(*e*) What is the rate constant, *k* (calculate from the slope of the line in *c*) ?

(*f*) Calculate the half-life from *k* and verify it with answer (*b*).

6.59. For a first order reaction it takes 5 minutes for the initial concentration of 0.6 mol L^{-1} to become 0.4 mol L^{-1}. How long will it take for the initial concentration to become 0.3 mol L^{-1}. (*C.B.S.E. 1993*)

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SOME IMPORTANT TERMS

- **Chemical kinetics.** The branch of chemistry which deals with the study of reaction rates and their mechanism.
- **Rate of reaction.** The rate of change of concentration of any of the reactant or product with time at any particular moment of time.
- **Rate constant (k).** It is the rate of the reaction when the concentration of each of reacting species is unity. It is also called *velocity constant* or *specific reaction rate* of the reaction.
- **Rate law.** The mathematical expression based on experimental fact, which describes the reaction rate in terms of concentrations of reacting species. It cannot be written from the balanced equation.
- **Molecularity.** The number of reacting particles which collides simultaneously to bring about the chemical change. It is a theoretical concept.
- **Order of reaction.** The sum of the exponents of the concentration terms in the experimental rate law of reaction. It can be zero, 1, 2, 3 or and any fractional value.
- **Half life period of reaction ($t_{1/2}$).** The time taken for the concentration of reactants to be reduced to half of their initial concentration.
- **Activation Energy (E_a).** The additional energy required by reacting species over and above their average PE to enable them to cross the energy barrier between reactants and products.
- **Activated complex.** The highly energetic arrangement of atoms formed during the course of reaction which corresponds to the peak of curve in the energy profile diagram for the progress of the reaction.
- **Photochemical reactions.** The chemical reactions in which the necessary activation energy to the reactants is provided by visible or u.v. light.
- **Photosensitization.** A process in which the photochemical reaction is initiated by addition of a foreign substance which is sensitive to radiation. The additional substance is called photosensitizer.

IMPORTANT FORMULAE

For the reaction $aA + bB \longrightarrow cC + dD$

- **Average rate** $= -\frac{1}{a}\frac{\Delta[A]}{\Delta t} = -\frac{1}{b}\frac{\Delta[B]}{\Delta t} = \frac{1}{c}\frac{\Delta[C]}{\Delta t} = \frac{1}{d}\frac{\Delta[D]}{\Delta t}$
- **Instantaneous rate** $= -\frac{1}{a}\frac{d[A]}{dt} = -\frac{1}{b}\frac{d[B]}{dt} = \frac{1}{c}\frac{d[C]}{dt} = \frac{1}{d}\frac{d[D]}{dt}$
- **Rate law.** Rate $= k[A]^m[B]^n$

  m and n are determined experimentally
- **Order w.r.t. A** $= m$; **Order w.r.t. B** $= n$
- **Overall order** $= m + n$
- **Units of rate** $= \text{mol L}^{-1}\text{ s}^{-1}$ or Atm s^{-1}
- **Units of k.** For reaction of **nth** order $k = (\text{mol L}^{-1})^{1-n}\text{ s}^{-1}$ or $(\text{atm})^{1-n}\text{ s}^{-1}$
- **Relation between k and t**

  For a *first order reaction*, $k = \frac{2.303}{t}\log\frac{[A]_0}{[A]}$

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For a *second order reaction*, $k = \frac{1}{t}\left[\frac{1}{[A]} - \frac{1}{[A]_0}\right]$

- **Half life period**

1st *order reaction*, $t_{1/2} = \frac{0.693}{k}$

nth *order reaction*, $t_{1/2} \propto \frac{1}{[A]_0^{n-1}}$

- **Amount after n half lives for 1st order reaction**
- $$[A]_n = [A]_0 (1/2)^n$$
- **Time of nth fraction of 1st order** $t_{1/n} = \frac{2.303}{k} \log\left(\frac{1}{1 - 1/n}\right)$
- **Arrhenious equation** $$k = Ae^{-E_a/RT}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\,R}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

EXERCISE

VERY SHORT ANSWER QUESTIONS
(1 Mark)

1. The instantaneous rate of reaction A ⟶ B is $-\frac{dA}{dt}$ or $\frac{dB}{dt}$. What is the significance of plus and minus sign ?
2. In what respects specific reaction rate differs from rate of the reaction.
3. For a chemical reaction X ⟶ Y, the rate increases by the factor 2.25 when concentration of X is increased by 1.5 suggest rate law and order.
4. Give the order of the reaction A ⟶ C whose rate quadruples when the concentration of A is doubled.
5. For a chemical reaction 2A + B ⟶ C, the rate of formation of C is 0.25 mol L^{-1} hr^{-1}. What is the rate of disappearance of A and B ?
6. For a chemical reaction A ⟶ H, the rate is found to increase by the factor 1.59 when conc. of A is doubled. What is the order ?
7. What is the order of the reaction having rate law expression as $r = k[A]^{3/2}[B]^{-1}$?
8. The rate expression for the chemical reaction $A_2 + B \longrightarrow C$ is $r = k[A_2]$. What is the possible mechanism ?
9. The rate constant of a reaction is found to have dimensions of mol L^{-1} sec^{-1}. What can be its order ?
10. A gas phase decomposition of *xy* follows the rate law $r = k[xy]^n$. What are the units of its rate constant ?
11. The value of rate constant of reaction at 25°C and 35°C are respectively 5×10^{-6} atm^{-1} sec^{-1} and 1.25×10^{-5} atm^{-1} sec^{-1}. What is the order of reaction and what is the value of temperature coefficient ?
12. A reaction is found to be zero order reaction, will its molecularity be zero ?
13. A chemical reaction is exothermic in nature, will it become faster or slower if temperature is increased ?
14. The reaction A + 3B ⟶ 2C obeys the rate equation :
rate $k[A]^{1/2}[B]^{3/2}$. What is the order of this reaction ?

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15. According to Arrhenius hypothesis, rate of reaction increases with increase in temperature. Give reasons. *(CBSE 1992)*

16. For a reaction, $X_2(g) + 2Y_2(g) \longrightarrow 2XY_2(g)$, write the rate equation in terms of the rate of disappearance of Y_2. *(A.I. CBSE 1992)*

17. The reaction $A + B \longrightarrow C$, has zero order. Write its rate equation. *(CBSE 1992)*

18. Why a photochemical change occurring in violet radiations does not take place in red radiations ?

19. For a reaction $NO_2 + CO \longrightarrow CO_2 + NO$, the rate law expression is rate $= k\,[NO_2]^2$. How many molecules are involved in slowest step ?

20. The rate law for the reaction is rate $= k\,[NO_2]^2[Cl_2]$ write, order w.r.t. Cl_2 ; order w.r.t. NO_2 and overall order of reaction. *(CBSE 1994)*

21. What are the units for the rate constant of 1st order reaction ? *(Har. Board 1995)*

22. Express the relationship between rate of production of water and the rate of disappearance of oxygen in the following reaction

$$2H_2 + O_2 \longrightarrow 2H_2O.$$

(CBSE 1995)

23. The rate of formation of a dimer in second order dimerisation reaction is 9.1×10^{-6} mol L^{-1} s^{-1} at 0.01 mol. L^{-1} monomer concentration. What is the value of rate constant ? *(CBSE 1995)*

24. How is the rapid change in concentrations of reactants/products monitored for fast reactions ? *(P.B. Board 1997)*

25. For a reaction, $A + H_2O \longrightarrow B$, the rate law is rate α [A]. What is
(*i*) its molecularity (*ii*) the order of reaction ? *(Pb. Board 1997)*

DESCRIPTIVE QUESTIONS
(2—3 Marks)

Rates of Chemical reaction

26. What is meant by the terms average and instantaneous rates of the reaction ? How are they expressed.

27. How can average and instantaneous rates of the reaction can be determined from the plot of concentration *vs* time ?

28. Give expressions for the rate of reaction $2X + 3Y \longrightarrow X_2Y_3$ in terms of rates of disappearance of the reactants and rates of appearance of the products.

29. Why can't rate of a reaction be obtained by dividing the total amount of reactant consumed with time taken ?

30. Express the rate of the reaction $3H_2(g) + N_2(g) \longrightarrow 2NH_3$ in terms disappearance of reactants and appearance of the product.

31. What do you understand by the rate of a chemical reaction ? Name the factor on which it depends.

32. Express the relationship between rate of production of iodine and the rate of disappearance of hydrogen iodide in the following reaction.

$$2HI \longrightarrow H_2 + I_2$$

(CBSE 1995)

Rate Law Order, Molecularity and Mechanism

33. Distinguish explicitly between rate of reaction and rate constant of the reaction. *(CBSE 1994)*

34. What are the factors on which rate constant of a reaction depends ?

35. In what respects does rate law differ from law of mass action ? Illustrate with the help of an example .

36. For each of the following reactions state the order w.r.t. to each reactant and also the overall order :
(*a*) $3NO(g) \longrightarrow N_2O(g) + NO_2(g)$; *rate* $= k[NO]^2$
(*b*) $H_2O_2 + 3I^- + 2H^+ \longrightarrow 2H_2O + I_3^-(aq)$; *rate* $= k\,[H_2O_2][I^-]$
(*c*) $CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$; *rate* $= k\,[CH_3CHO]^{3/2}$
(*d*) $CHCl_3(g) + Cl_2(g) \longrightarrow CCl_4(g) + HCl(g)$; *rate* $= k\,[CHCl_3][Cl_2]^{1/2}$

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(*e*) $C_2H_5Cl(g) \longrightarrow C_2H_4(g) + HCl(g)$; *rate* = $k\,[C_2H_5Cl]$

What are the dimensions of the rate constant in each case ?

37. How does order of the reaction differ from the molecularity ? ***(Pb. Board 1994)***

38. The reaction, $A + 2B \longrightarrow C + D$, obeys the rate equation ; Rate = $k[A]^x[B]^y$. What would be the order of the reaction ? ***(CBSE 1993)***

39. Write the general expression for the rate constant, k, for a first order reaction and show how to derive from it the expression $k = 0.693/t_{1/2}$.

40. What is $t_{1/2}$? Give expression relating time required for nth fraction of reactant of disappear to the rate constant of first order reaction.

41. The first order decomposition of SO_2Cl_2 into SO_2 and Cl_2 presumably proceeds by a two step mechanism

(*a*) write a reasonable mechanism for the reaction

(*b*) which step is the rate determining step.

42. Deduce the rate law expressions for the conversion of H_2 and I_2 to HI at 400°C, corresponding to each of the following mechanisms :

(*a*) $H_2 + I_2 \longrightarrow 2HI$ (one step) (*b*) $I_2 \rightleftharpoons 2I$; $2I + H_2 \longrightarrow 2HI$ (slow)

(*c*) $I_2 \longrightarrow 2I$; $I + H_2 \rightleftharpoons IH_2$; $IH_2 + I \longrightarrow 2HI$ (slow).

43. Nitric oxide, NO, reacts with oxygen to produce nitrogen dioxide :

$$2NO(g) + O_2(g) \longrightarrow 2NO_2(g)$$

What is the predicted rate law, if the mechanism is

$$NO + O_2 \overset{K}{\rightleftharpoons} NO_3\ (fast)$$

$$NO_3 + NO \xrightarrow{k_1} NO_2 + NO_2\ (slow).$$

44. What is half-life period of the reaction show that for the first order reaction $t_{1/2}$ is independent of initial concentration ? ***(Pb. Board 1991 ; H.P. Board, 1993)***

45. Name the methods to determine the order of the reactions.

46. What is $t_{1/2}$? How it is related to $t_{3/4}$ and $t_{7/8}$?

47. If C_0 is the initial concentration of the reactant in a first order reaction and C_n is the concentration after n half-lives. What is the relationship between C_0 and C_n ?

48. The following mechanism has been proposed for the reaction

$$A + C \longrightarrow D + F\ (slow)$$

$$F + B \longrightarrow E\ (fast)$$

Write down the rate expression and overall reaction.

49. For the reaction $2NO_2 + F_2 \longrightarrow 2NO_2F$, the rate law is given by

$$r = k\,[NO_2]\,[F_2]$$

Suggest a suitable mechanism based upon the above rate law indicating the rate determining step. Had the reaction been the single step reaction what would have been its rate law.

50. What do you mean by pseudo monomolecular reaction ? Give example. ***(Pb. Board 1997)***

51. The rate expression for the chemical reaction $2NO_2F \longrightarrow 2NO_2 + F_2$ is

$$r = k\,[NO_2F]$$

(*i*) Propose a suitable mechanism for the reaction

(*ii*) What should be the units of rate constant ?

52. Give the units of rate constant of 1st order, 2nd order, 3rd order and nth order reaction.

53. What is a first order reaction ? Give two examples ?

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54. Derive expression for the rate constant of the first order reaction. Show that log [A] is a linear function of time.
55. How can the plot of *log* [*A*] and *t* be used for the calculation of rate constant for the first order ?
56. What would be the probable plot of *conc. vs.* time for zero order reaction ?
57. The rate expression for a homogeneous reaction

$$2NO_2Cl(g) \rightleftharpoons 2NO_2(g) + Cl_2(g) \text{ is given by}$$
$$\text{Rate} = k[NO_2Cl]$$

Suggest the mechanism for the reaction.

58. Discuss giving diagram the time dependence of the concentration of reactants and products in a chemical reaction.
59. The gas phase decomposition of acetaldehyde

$$CH_3CHO(g) \longrightarrow CH_4(g) + CO(g)$$

at 680 K is observed to follow the rate expression :

$$\text{rate} = -d\,[CH_3CHO]/dt = k\,[CH_3CHO]^{3/2}$$

If the rate of the decomposition is followed by monitoring the partial pressure of the acetaldehyde, we can express the rate as

$$-dP_{CH_3CHO}/dt = k[P_{CH_3CHO}]^{3/2}$$

If the pressure is measured in atmosphere and time in minutes, then

(*a*) What are the units of the rate of the reaction ?

(*b*) What are the units of the rate constant, *k* ?

60. The initial rate of the reaction

$$A + B_2 \longrightarrow C_2 + D,$$

is doubled if the initial concentration of A is doubled, but is quadrupled if the initial concentration of B_2 is doubled :

(*a*) What is the order with respect to each of the reactants ?

(*b*) What is the overall order of the reaction ?

(*c*) Could this possibly be a single step reaction ? Explain.

Activation Energy, Arrhenious Equation

61. What is temperature coefficient of the reaction ? What is the meaning of the statement that temperature coefficient of a reaction is 2.1 ?
62. Explain the following :

(*i*) Activation energy (*i*) Threshold energy (*iii*) Activated complex.

63. Write Arrhenius equations for the rate constants k_1 and k_2 corresponding to temperature T_1 and T_2. Use the two expressions to determine the value of activation energy.
64. Justify the following statements :

(*i*) Reactions with low activation energy are fast while those with high activation energy are slow.

(*ii*) The reaction rate almost doubles for 10° rise in temperature although the collision frequency does not change appreciably.

65. What is activation energy ? How is the rate constant of a reaction is related to activation energy ? ***(CBSE 1990)***
66. What is activated complex ? How does it differ from : (*a*) ordinary molecule (*b*) reaction intermediate ?
67. Why do different reactions proceed with different rates ?
68. What makes us possible to store fuels safely in the presence of oxygen ?

Photochemical Reactions

69. What are photochemical reactions ? Explain the mechanism of photosynthesis of HCl. ***(CBSE 1992)***
70. Give two examples of : (*i*) fast reactions and (*ii*) photochemical reactions.

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71. Explain the following :

(*i*) The rate of chlorination of methane is accelerated by light.

(*ii*) The diffused freon in the ozone layer causes its destruction.

(*iii*) The rate of zero order reaction does not change with time.

72. Point out important differences between, thermal reactions and photochemical reactions.

73. What is photosensitization ? Explain it with the help of an example. *(CBSE 1993)*

SOME MISCELLANEOUS QUESTIONS

74. Is there any reaction whose rate does not fall with the progress of reaction ?

75. Give example of a reaction whose rate increases with the progress of the reaction.

76. What value of k is predicted for the rate constant by Arrhenius equation if T approaches ∞. Is the value physically reasonable ?

77. Show that time required for first order reaction to go 99.9% completion is 10 times the half-life period.

78. What is meant by photosensitizer ? What is its role in photosensitized reaction ?

79. Give importance of photochemical reactions in daily life. Is there any damaging effect of photochemical reactions ?

80. What role is played by chlorophyll during photosynthesis in plants ?

81. Can we measure the rates of fast reactions by ordinary means ? Give the names of some techniques which are employed for this purpose.

82. Define the term activation energy. How does catalyst affect it. Explain with the help of diagram.

83. Explain why, the order and molecularity have different values for the following reaction

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

84. Draw the probable energy profile diagram for the progress of reaction whose mechanism is :

$$A_2 + B \longrightarrow A_2B \ (slow)$$
$$A_2B \longrightarrow AB + A \ (fast)$$

85. How is rate constant related to concentrations of the reactants ? *(CBSE 1994)*

86. Define the reaction rate. For the reaction $N_2(g) + 3H_2(g) \longrightarrow 2NH_3(g)$, how is the rate of formation of ammonia related to the rate of disappearance of hydrogen ? How is the order of this reaction influenced if nitrogen is present is large excess ? *(CBSE 1992)*

87. Express the rate of reaction, $2N_2O_5 \longrightarrow 2NO_2 + O_2$, using concentration changes of N_2O_5 and O_2. *(Pb. Board 1995)*

NUMERICAL PROBLEMS

88. A certain reaction, $X + Y \longrightarrow$ Products, is first order w.r.t. each reactant with $k = 5 \times 10^{-3}$ L mol^{-1} s^{-1}. Calculate the concentration of X remaining after 100 sec. if initial concentration of X was 0.100 M and that of Y was 10 M. State any approximation that you will make in obtaining the result.

89. Write stoichiometric equation whose mechanism is detailed below

$$A_2 \rightleftharpoons 2A; \quad k_f = 10^{10}\ s^{-1}, k_b = 10^{10}\ M^{-1}s^{-1}$$
$$A + C \longrightarrow AC; \quad k = 10^{-4}\ M^{-1}\ s^{-1}$$

So write (*i*) Value of equilibrium constant for the first step

(*ii*) Rate law equation for the overall reaction in terms of initial concentrations.

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90. The rate constant for the decomposition of N_2O_5 at various temperatures are :

$t°C$	*Rate constant, k* (s^{-1})
0	7.87×10^{-7}
20	1.70×10^{-5}
40	2.57×10^{-4}
60	1.78×10^{-3}
80	2.14×10^{-2}

Plot log k against 1/T and calculate the energy of activation. Predict the reaction rate at 303 K, 323 K and 343 K.

91. The reaction $2NO(g) + Cl_2(g) \rightleftharpoons 2NOCl$ was studied at – 10°C, and the following data were obtained :

Run	*Initial Concentrations* ($mol\ L^{-1}$) [NO]	[Cl_2]	*Initial Rate of Formation of NOCl* ($mol\ L^{-1}\ min^{-1}$)
1	0.10	0.10	0.18
2	0.10	0.20	0.36
3	0.20	0.20	1.44

(*a*) What is the order of reaction with respect to NO and with respect to Cl_2 ?

(*b*) What is the numerical value of the rate constant at – 10° C ?

92. The inversion of sucrose was studied in 1 M HCl at 298 K. The following data were obtained for optional rotation at different time intervals

Time (Min.)	0.0	10.0	20.0	30.0	∞
Rotation (degrees)	24.5	22.3	20.3	18.4	– 10.7

Calculate (*i*) Rate constant of the reaction, and (*ii*) half-life period.

Also show that the reaction follows the first order kinetics.

93. The decomposition of Cl_2O_7 at 400 K in the gas phase to Cl_2 and O_2 is 1st order reaction.

(*i*) After 55 seconds at 400 K, the pressure of Cl_2O_7 falls from 0.062 to 0.044 atm. Calculate the rate constant.

(*ii*) Calculate the pressure of Cl_2O_7 after 100 sec of decomposition at this temperature. **(*Roorkee 1989*)**

94. The rate of decomposition of N_2O_5 is 1.3×10^{-4} mol L^{-1} s^{-1} when [N_2O_5] concentration is 0.22 M. What is the value of k for this first order reaction ? **(*B.I.T. Ranchi 1992*)**

95. A gas phase decomposition of dimethyl ether follows the first order kinetics

$$CH_3—O—CH_3(g) \longrightarrow CH_4(g) + H_2(g) + CO(g)$$

The reaction is carried out in a constant volume container at 500°C and has a half-life period of 14.5 min. Initially only dimethyl ether is present at a pressure of 0.40 atmosphere. What is the total pressure of the system after 12 min ? Assume ideal behaviour. **(*IIT 1993*)**

96. Show that for the first order reaction the value of $t_{3/4}$ is twice the value of $t_{1/2}$.

97. A first order reaction $A \longrightarrow B$ requires activation energy of 70 kJ mol^{-1}. When 20% solution of A was kept at 25°C for 20 minutes, 25% of decomposition took place what will be the percentage decomposition of 30% solution at 40°C in the same time. Assume activation energy remains constant in this range of temperature. **(*IIT 1993*)**

98. The half time for the decomposition of nitramide is 2.1 hour at 15°C

$$NH_2NO_2(aq) \longrightarrow N_2O(g) + H_2O(l)$$

If 6.2 g of NH_2NO_2 is allowed to decompose, calculate :

(*i*) time taken for NH_2NO_2 to decompose 99%

(*ii*) volume of dry N_2O produced at this point measured at N.T.P. **(*Roorkee 1994*)**

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99. Consider the data for the reaction between A and B

[A] (mol L^{-1})	[B] (mol L^{-1})	Initial rate (mol L^{-1} s^{-1})	
		At 300 K	At 320 K
2.5×10^{-4}	3.0×10^{-5}	5×10^{-4}	2×10^{-3}
5.0×10^{-4}	6.0×10^{-5}	4×10^{-3}	—
1.0×10^{-3}	6.0×10^{-5}	1.6×10^{-2}	—

Calculate (*i*) order w.r.t. A and B (*ii*) rate constant at 300
(*iii*) the energy of activation (*iv*) the pre-exponential factor. *(IIT 1994)*

100. The progress of the reaction $A \rightleftharpoons nB$ with time is represented by the Fig. 6.15. Determine.

(*i*) the value of *n*.
(*ii*) the equialibrium constant K
(*iii*) the initial rate of disappearance of A. *(IIT 1994)*

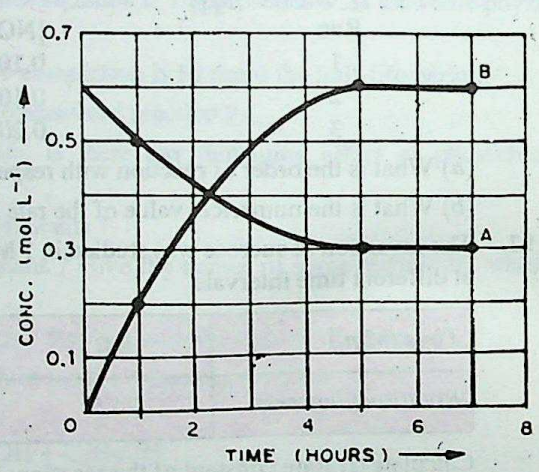

Fig. 6.15

101. The rate constant of a first order reaction becomes 6 times when the temperature is increased from 350 K to 410 K. Calculate the energy of activation for the reaction. (R = 8.314 JK^{-1} mol^{-1}). *(CBSE 1995)*

102. Consider the following data for the reaction

$$A + B \longrightarrow \text{Products}$$

Conc. of A (mol L^{-1})	Conc. of B (mol L^{-1})	Initial Rate (mol L^{-1} s^{-1})
0.1	0.1	4.0×10^{-4}
0.2	0.2	1.6×10^{-3}
0.5	0.1	1.0×10^{-2}
0.5	0.5	1.0×10^{-2}

Calculate :

(*i*) the order w.r.t. A and B for the reaction
(*ii*) the rate constant
(*iii*) the reaction rate when the concentrations of A and B are 0.2 M and 0.35 M respectively. *(Roorkee 1995)*

103. At 380°C, the half-life period for the first order decomposition of H_2O_2 is 360 min. The energy of activation of the reaction is 200 kJ mol^{-1}. Calculate the time required for 75% decomposition at 450°C. *(IIT. 1995)*

104. The ionisation constant of NH_4^+ ion in water is 5.6×10^{-10} at 25°C. The rate constant for the reaction between NH_4^+ and OH^- to form NH_3 and H_2O at 25°C is 3.4×10^{10} L mol^{-1} s^{-1}. Calculate the rate constant for proton transfer from H_2O to NH_3. *(IIT 1996)*

105. The rate constant for the first order decomposition of certain reaction is described by the equation

$$\log k(s^{-1}) = 14.34 - \frac{1.25 \times 10^4 \text{ K}}{T}$$

(*i*) What is the energy of activation for this reaction ?
(*ii*) At what temperature will the half life period be 256 minutes ? *(ITT 1997)*

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106. Consider the following data for the reaction A + B ⟶ Products

Run	*Initial conc. of A*	*Initial conc. of B*	*Initial rate* ($mol\ L^{-1}\ sec^{-1}$)
1	0.1 M	1.0 M	2.1×10^{-3}
2	0.2 M	1.0 M	8.4×10^{-3}
3	0.2 M	2.0 M	8.4×10^{-3}

Determine overall order, order with respect to A and that with respect to B. **(*CBSE 1997*)**

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select the correct answer from each of the following questions :

1. For a chemical reaction, $x + 2y \longrightarrow z$, if the rate of appearance of z is 0.50 moles per litre per hour, then the rate of disappearance of y is
(*a*) 0.5 mol L^{-1} hr^{-1} (*b*) 1.0 mol L^{-1} hr^{-1} (*c*) 0.25 mol L^{-1} hr^{-1} (*d*) cannot be predicted.

2. For the reaction, $NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$, the correct expression for the rate of the reaction is
(*a*) rate = $\frac{-d[NO_2]}{dt}$ (*b*) rate = $\frac{-d[CO_2]}{dt}$ (*c*) rate = $\frac{d[NO_2] - d[CO]}{dt}$ (*d*) rate = $\frac{d[CO_2]}{dt}$.

3. The rate of a reaction is primarily determined by the slowest step. This step is called
(*a*) rate determining step (*b*) activation step (*c*) reaction rate step (*d*) none of these.

4. The reactions of high molecularity are rare because
(*a*) Many body collisions have a low probability
(*b*) Many body collisions are not favoured energetically
(*c*) Activation energy of many body collisions is very large.
(*d*) Very high concentration is required for such reactions.

5. For a chemical reaction $A \longrightarrow B$, it is found that the rate of the reaction quadruples when the concentration of A is doubled. The rate expression for the reaction is, rate = $k[A]^n$ where the value of n is
(*a*) 1 (*b*) 2 (*c*) 0 (*d*) 3.

6. On increasing the temperature of the reacting system by 10° the rate of reaction almost becomes double. The most appropriate reason for this is that
(*a*) Activation energy decreases by increase of temperature
(*b*) The fraction of molecules having threshold energy increases
(*c*) Collision frequency increases (*d*) The value of threshold energy decreases.

7. The half-life period of any first order reaction
(*a*) is half the specific rate constant (*b*) is always the same irrespective of the reaction
(*c*) is independent of initial concentration (*d*) is directly proportional to initial concentration reactants.

8. The dimensions of rate constant of 2nd order reaction involves
(*a*) concentration (*b*) concentration and time
(*c*) time only (*d*) neither time nor concentration.

9. A zero order reaction $A \longrightarrow$ *Products*, has rate constant 10^{-2} mol L^{-1} s^{-1}. If a process is started with 10 moles of A in a one litre vessel, the number of *moles* of reactant after 10 minutes will be
(*a*) 10 (*b*) 5 (*c*) 6 (*d*) 4.

10. For which of the following reactions, the temperature coefficient is maximum ?
(*a*) $A \longrightarrow B$; $E_a = 50$ kJ (*b*) $P \longrightarrow Q$; $E_a = 40$ kJ
(*c*) $X \longrightarrow Y$; $E_a = 60$ kJ (*d*) $W \longrightarrow Z$; $E_a = 80$ kJ.

11. A hypothetical reaction $2p + q \longrightarrow s + r$ has rate constant as 2.0×10^{-3} mol L^{-1} s^{-1}. The order of the reaction is
(*a*) unpredictable (*b*) zero (*c*) one (*d*) two.

12. The ratio $t_{7/8} : t_{1/2}$ for the first order reaction is
(*a*) 3 (*b*) 5 (*c*) 2 (*d*) 7.

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13. The molecularity of the reaction cannot be
(a) 1 (b) 2 (c) 1.5 (d) 3.

14. For the first order reaction, the half-life is independent of
(a) catalyst (b) temperature
(c) both catalyst and temperature (d) initial concentration of reactants.

15. For a certain reaction $aA \longrightarrow bB$, the rate of reaction is doubled when the concentration of A is increased by four times. The rate of reaction is equal to
(a) $k[A]^a$ (b) $k[A]^{1/2}$ (c) $k[A]^{1/a}$ (d) $k[A]$.

16. The rate law for the chemical reaction, $2NO_2Cl \longrightarrow 2NO_2 + Cl_2$ is $r = k[NO_2Cl]$. Which of the following is rate controlling step ?
(a) $NO_2 + Cl \longrightarrow NO_2Cl$ (b) $NO_2Cl + Cl \longrightarrow NO_2 + Cl_2$
(c) $NO_2Cl \longrightarrow NO_2Cl$ (d) $2NO_2Cl \longrightarrow 2NO_2 + Cl_2$.

17. If a graph is plotted between $\ln k$ and $1/T$ for the first order reaction, the slope of the straight line so obtained is given by
(a) $-E_a/R$ (b) $-E_a/2.303\,R$ (c) $-\frac{2.303}{E_aR}$ (d) $-\frac{E_a}{2.303}$.

18. For a first order reaction, $A \longrightarrow$ *products*, if k is the rate constant then the half life period of the reaction is equal to
(a) $\frac{0.693}{k[A]}$ (b) $\frac{1}{k}\frac{1}{[A]}$ (c) $\frac{1}{k}\ln\frac{[A]}{[A]_0}$ (d) $\frac{\ln 2}{k}$.

19. A first order reaction has a half life period of 34.65 seconds. Its rate constant is
(a) $2 \times 10^{-2}\ s^{-1}$ (b) $4 \times 10^{-2}\ s^{-1}$ (c) $20\ s^{-1}$ (b) $2 \times 10^{-2}\ s^{-1}$.

20. For the reaction, $2x + y \longrightarrow z$, the following kinetic data was obtained :

$[x]$ $(mol\ L^{-1})$	$[y]$ $(mol\ L^{-1})$	$\frac{d[z]}{dt}$ $(mol\ L^{-1}\ s^{-1})$
4.0	1.0	1.0
4.0	4.0	2.0
1.0	4.0	1.0

The rate expression is :
(a) $k[x][y]^{1/2}$ (b) $k[x]^2[y]$ (c) $k[x]^{1/2}[y]^{1/2}$ (d) $k[x]^{1/2}[y]$.

21. The temperature dependence of the rate constant is given by the Arrhenius equation
(a) $\ln k = 1\ln A - \frac{E_a}{RT}$ (b) $\ln A = \ln k - \frac{E_a}{RT}$
(c) $\ln k = A\frac{E_a}{RT}$ (d) $\ln A = RT \ln E_a - \ln k$.

22. The large increase in rate of a reaction on rise in temperature is due to
(a) the decrease in activation energy barrier
(b) the increase in collision frequency
(c) the increase in the fraction of molecules having energy ≥ the threshold energy
(d) the increase in kinetic energy of molecules.

23. For a hypothetical reaction, $2A + 2B \longrightarrow X + Y$, the kinetic data revealed the rate expression, rate $= k[A]^2[B]$. If the reaction proceeds by the following sequence of steps :
Step I $A + B \longrightarrow C$
Step II $A + C \longrightarrow D$

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Step III $B + D \longrightarrow X + Y$

then the rate determining step is

(*a*) Step I (*b*) Step II

(*c*) Step III (*d*) cannot be predicted as data is insufficient.

24. The mechanism of $2O_3 \longrightarrow 3O_2$ is given as

$$O_3 \rightleftharpoons O_2 + O \text{ (Fast)}$$

$$O + O_3 \rightleftharpoons 2O_2 \text{ (Slow)}$$

which of the following represents the rate law ?

(*a*) $r = k[O_3]^2$ (*b*) $r = k[O_3]^2[O_2]^{-1}$ (*c*) $r = k[O_3][O_2]$ (*d*) unpredictable.

25. For a reaction, $E_a = 0$ and $k = 4.2 \times 10^5\ s^{-1}$ at 300 K. The value of k at 310 K will be

(*a*) 4.2×10^5 (*b*) 8.4×10^5 (*c*) 8.4×10^{10} (*b*) unpredictable.

26. For a chemical reaction $xA \longrightarrow yM$ the rate law is $r = k[A]^3$. If the concentration of A is doubled the reaction rate will be

(*a*) doubled (*b*) quadrupled (*c*) increase by 8 times (*d*) unchanged.

27. For a certain first order reaction, $X \longrightarrow Y + Z$, the value of $t_{1/2}$ is 10 minutes. The concentration of X is reduced to 10% of the original concentration in

(*a*) 10 min (*b*) 90 min (*c*) 33 min (*d*) 70 min.

28. The reactions with low activation energy are

(*a*) always spontaneous (*b*) slow (*c*) non-spontaneous (*d*) fast.

29. For a reaction with $E_a = 20.0$ kJ the value of k at 300 K is $6.4 \times 10^4\ s^{-1}$ the value of k at 310 K is

(*a*) $6.4 \times 10^4\ s^{-1}$ (*b*) $3.2 \times 10^4\ s^{-1}$

(*c*) $1.56 \times 10^4\ s^{-1}$ (*d*) 3.2×10^5 s.

30. Which of the following produces a change in the value of rate constant of a reaction

(*a*) concentration (*b*) pressure

(*c*) temperature (*d*) catalyst.

31. In the first order reaction, 75% of the reactant disappeared in 1.38 h, the rate constant of the reaction is

(*a*) $3.6 \times 10^{-3}\ s^{-1}$ (*b*) $2.8 \times 10^{-4}\ s^{-1}$

(*c*) $17.2 \times 10^{-3}\ s^{-1}$ (*d*) $1.8 \times 10^{-5}\ s^{-1}$. ***(ISM. Dhanbad 1994)***

32. Diazonium salt decomposes as $C_6H_5N_2^+Cl^- \longrightarrow C_5H_5Cl + N_2$

The evolution of N_2 becomes two times faster when the initial concentration of salt is doubled. The order of reaction is

(*a*) 1 (*b*) 2 (*c*) 3 (*d*) zero. ***(MLNR 1994)***

33. The rate constant, activation energy, and Arrhenius parameter of a chemical reaction at 25°C are $3.0 \times 10^{-4}\ s^{-1}$, 104.4 kJ mol^{-1} and $6.0 \times 10^{14}\ s^{-1}$ respectively. The value of the rate constant as $T \longrightarrow \infty$ is :

(*a*) $2 \times 10^{18}\ s^{-1}$ (*b*) $6.0 \times 10^{14}\ s^{-1}$ (*c*) infinity (*d*) $6.0 \times 10^{30}\ s^{-1}$.

(IIT 1996)

34. In a reversible reaction, $2NO_2 \underset{k_2}{\overset{k_1}{\rightleftharpoons}} N_2O_4$, the rate of disappearance of NO_2 is equal to

(*a*) $\dfrac{2k_1[NO_2]^2}{k_2}$ (*b*) $2k_1[NO_2]^2 - 2k_2[N_2O_4]$

(*c*) $k_1[NO_2]^2 - k_2[N_2O_4]$ (*d*) $(2k_1 - k_2)[NO_2]$. ***(CEET Kurukshetra 1996)***

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ASSERTION REASON TYPE QUESTIONS

In each of the following questions two statements are given one of the statement is lablled as ***Assertion* A** and the other one as ***Reason* R**. Read the statements carefully and mark correct choice (*a*), (*b*), (*c*) or (*d*) according to the following instructions.

(*a*) If both A and R are correct and R is a correct reason of A

(*b*) If both A and R are correct but R is not the explanation of A

(*c*) If A is correct and R is wrong

(*d*) If A is wrong and R is correct.

35. ***Assertion* 'A'** : Half-life period is always independent of initial concentration.

***Reason* R** : Half-life period in inversely proportional to rate constant.

(*a*) (*b*) (*c*) (*d*)

36. ***Assertion* 'A'** : ΔG for photochemical spontaneous reaction may or may not be – ve.

***Reason* R** : In photochemical reactions, the activation energy to reactants is provided by light.

(*a*) (*b*) (*c*) (*d*)

37. ***Assertion* A** : The rate of reaction can also increase with its product if one of the product act as catalyst.

***Reason* R** : A catalyst lowers the activation energy of reactions.

(*a*) (*b*) (*c*) (*d*)

38. ***Assertion* A** : In zero order reaction, the *conc.* vs *time* graph is a straight time.

***Reason* R** : The rate of change of conc. per unit time in zero order reaction remains constant.

(*a*) (*b*) (*c*) (*d*)

39. ***Assertion* A** : The order of a reaction is always whole number.

***Reason* R** : The molecularity of a reaction is a whole number other than zero, but generally less than 3.

(*a*) (*b*) (*c*) (*d*)

40. ***Assertion* A** : Order of a reaction cannot be written from the balanced equation.

***Reason* R** : Rate law can provide some clue about the reaction mechanism.

(*a*) (*b*) (*c*) (*d*)

FILL IN THE BLANKS

Fill in the blanks with appropriate items :

1. Hydrolysis of ethyl acetate in an acidic solution is an example of ..... order.
2. If the activation energy of the reaction is low, it proceeds at ..... rate.
3. The reaction taking place under the influence of visible light is called ..... reaction.
4. In a multi-step reaction, the ..... step determines the rate of the reaction.
5. The sum of powers to which the concentration terms are raised in the rate law is called ..... of the reaction.
6. For a first order reaction, the half life period is equal to .....
7. The order of a reaction with respect to B, whose rate law is, rate = $k[A]^{3/2}[B]^{1/2}$ is .....
8. The order and molecularity of a complex reaction ..... be same.
9. In photochemical reactions, the necessary activation energy is provided by .....
10. The units of rate of gaseous reaction are .....
11. Temperature coefficient = ...
12. For a zero order reaction A → Products, the plot of [A] vs time has a slope = ...

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13. Rate law ..... be written from the balanced equation of the reaction.
14. $t_{1/2}$ of certain reaction is inversely proportional to the square of concentration of the reactant. The order of the reaction is .....
15. For the reaction $xA + yB \longrightarrow lL + mM$, the average rate of disappearance of B = ...
16. In the Arrhenius equation, $k = A\,exp\,(-E/RT)$, A may be termed as rate constant at ..... *(IIT. 1997)*

TRUE/FALSE STATEMENTS

Pick up True or False statements out of the following :

1. When Δt is infinitesimally small, the average rate equals the instantaneous rate.
2. The reaction rate constant, k for a given reaction varies directly as the rate varies.
3. The speed of any chemical reaction is directly proportional to the molar concentrations.
4. In a rate equation, the power to which the concentrations are raised cannot be determined by inspection of the balanced equation.
5. A chain reaction, once started, cannot be stopped till it is complete.
6. The value of ΔG for spontaneous photochemical reaction should be < 0.
7. The rate constant of a first order reaction whose $t_{1/2}$ is 6.93 s will be $10\ s^{-1}$.
8. With the increase in temperature, the value of k for endothermic reactions decreases.
9. Order of a reaction increases with the rise in temperature.
10. For a second order reaction, the slope of graph between *rate* and $(conc.)^2$ is equal to k.
11. The dimensions of pre exponential factor A in the Arrhenius equation for second order reaction are $L\ mol^{-1}\ s^{-1}$.
12. The increase in the rate of reaction by increasing the temperature by 10° is due to the increase in the total number of collisions between the reacting particles.
13. Molecularity of the reaction is always a whole number greater than zero.
14. The combustion reactions are highly exothermic, and therefore, their activation energy is zero.
15. The rates of photochemical reactions, generally depends upon the intensity of radiation.

MATCHING THE COLUMNS

Match the items given in Column A to those given in Column B and C

A	B	C
1. First order reaction.	1. $\neq 1$.	1. Can be zero, whole number or fractional value.
2. Number of reacting particles which collide simultaneously to bring about chemical change.	2. Generally high for thermal reactions.	2. Reactions initiated by light.
3. Order of reaction.	3. s^{-1}.	3. $k_{310} : k_{300}$.
4. Temperature coefficient.	4. May have $\Delta G > 0$ or < 0.	4. Molecularity.
5. Photochemical reactions.	5. Sum of the exponents of concentration terms in rate law.	5. $t_{1/2} = \frac{0.693}{k}$ sec.

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ANSWERS/HINTS

REVIEW PROBLEMS

6.2. (*i*) 4.0×10^{-13} mol L^{-1} s^{-1} (*ii*) 2.0×10^{-13} mol L^{-1} s^{-1}

6.3. 1×10^{-3} mol L^{-1} s^{-1} ; 2.0×10^{-3} mol L^{-1} s^{-1}

[**Hint.** Rate of reaction $= \dfrac{\Delta[NO_2]}{4\Delta t}$

Rate *g* disappearance of $N_2O_5 = \dfrac{1}{2} \times$ Rate of appearance of NO_2

or $\dfrac{-\Delta[N_2O_5]}{\Delta t} = \dfrac{1}{2} \times \dfrac{\Delta[NO_2]}{\Delta t} = \dfrac{1 \times 20 \times 10^{-3}}{2 \times 5} = 2 \times 10^{-3}$ mol L^{-1} s^{-1}]

6.4. Reaction rate $= -\dfrac{4}{5} \times \dfrac{\Delta[O_2]}{\Delta t} = \dfrac{4}{6} \times \dfrac{\Delta[H_2O]}{\Delta t}$

6.5 $-\dfrac{\Delta[I^-]}{\Delta t} = 0.006$ mol L^{-1} min^{-1} ; $\dfrac{\Delta[I_2]}{\Delta t} = 0.003$ mol L^{-1} min^{-1} **6.6.** 0.012 min.

6.7. 0.002 atm min^{-1} ; 8.58×10^{-7} mol L^{-1} s^{-1}

[**Hint.** The increase in pressure (133 – 114) mm refers to increase in concentration of O_2.]

6.8. $NO_2Cl \longrightarrow NO_2 + Cl$ (*slow*) ; $NO_2Cl + Cl \longrightarrow NO_2 + Cl$ (*fast*)

6.9. $(CH_3)_3CCl \longrightarrow (CH_3)_3C^+ + Cl^-$ (*slow*) ; $(CH_3)_3C^+ + OH^- \longrightarrow (CH_3)_3C—OH$ (*fast*)

6.10. $N_2O_5 \longrightarrow NO_2 + NO_3$ (*slow*)
$N_2O_5 + NO_3 \longrightarrow 2NO_2 + O_2$ (*fast*)

6.11. $HBr + O_2 \longrightarrow HOOBr$ (*slow*)
$HOOBr + HBr \longrightarrow 2HOBr$ (*fast*)
$HOBr + HBr \longrightarrow H_2O + Br$ (*fast*)

6.12. Rate $= k[H_2][I_2]$

6.13. 3.5×10^{-4} mol L^{-1} min^{-1}, 8.8×10^{-5} mol L^{-1} min^{-1}

6.14. (*a*) 7.75×10^{6} mol L^{-1} s^{-1} (*b*) 9.3×10^{-6} mol L^{-1} s^{-1} (*c*) 3.87 mol L^{-1}

6.15. Rate $= k\,[NO]^2[Cl_2]$

6.16. Rate $= k[A][B]^2$, $k = 3.0 \times 10^{-2}$ mol^{-2} L^2 min^{-1}

6.17. Rate $= k[Cl_2][NO]^2$, $k = 1.20 \times 10^{2}$ mol^{-2} L^2 s^{-1}

6.18. Rate $= k\,[A][B]^2$; Overall order = 3 ; L^2 mol^{-2} min^{-1}

6.19. 4×10^{-9} mol L^{-1} s^{-1} ; 1.28×10^{-10} mol L^{-1} s^{-1}

6.20. $k = 8.6 \times 10^{-4}$ min^{-1}

6.21. 0.0197 min^{-1}

6.22. $k = 1.048 \times 10^{-3}$ s^{-1}

6.23. 0.00426 min^{-1}

6.24. 0.0102 min^{-1} ; 157.6 min

6.29. 5.55×10^{-2} hr^{-1}

6.30. 38.4 min.

6.31. 300 sec.

6.32. 158.5 sec

6.34. 25 min ; 2.77×10^{-2} min^{-1}

6.35. 0.122 hr^{-1} ; 18.94 hr

6.36. 2.01×10^{3} sec.

6.37. 6.25%

6.38. 188 sec.

6.39. 9.38×10^{3} sec.

6.40. 7.7×10^{-5} sec^{-1}

6.41. 84.96 kJ mol^{-1}

6.42. $E_a = 54.60$ kJ mol^{-1} ; $A = 2.01 \times 10^{5}$ L mol^{-1} s^{-1}

6.43. $E_a = 209$ kJ mol^{-1}

6.44. 50.48 kJ mol^{-1}

6.45. 53.59 kJ mol^{-1}

6.46. 52.87 kJ mol^{-1}

6.47. 103 kJ mol^{-1}

6.48. 5.63×10^{-3} min^{-1} ; 409 min

6.49. 4 min ; 6.65 min

6.50. 8.7×10^{-3} s^{-1}, 33 s, 219 s

6.51. 1.25 g ; 0.156 g

[**Hint.** $C_n = C_0 \times 2^{-n}$; C_n = concentration after *n* half lives
C_0 = initial concentration]

6.52. 90.9 min

6.54. $k = 0.01386$ s^{-1} ; rate $= 5.54 \times 10^{-4}$ atm s^{-1}

6.56. 55 times.

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VERY SHORT ANSWER QUESTIONS

2. Specific reaction rate is the rate of reaction at unit concentration of each of reactant. It is always constant for a particular reaction at a given temperature.

3. $r = k[X]^2$; order is 2 **4.** rate law is $r = k[A]^2$; order is 2

5. $A = -0.5$ mol L^{-1} hr^{-1}, $B = -0.25$ mol L^{-1} hr^{-1} **6.** 2/3

7. 0.5 **8.** $A_2 \longrightarrow A + A$ (slow); $2A + B \longrightarrow C$ (fast)

9. zero **10.** $atm^{(n-1)}$ sec^{-1} **11.** second; temp. co-eff. = 2.5

12. NO, molecularity cannot be zero. **13.** faster

14. 2 **16.** rate $= -\frac{1}{2}\frac{d[Y_2]}{dt}$ **17.** rate $= k[A]^{\circ}[B]^{\circ}$

18. The photons of red radiation, are not able to provide sufficient activation energy to cause excitation of reacting molecules

19. Two **20.** Order w.r.t. $Cl_2 = 1$; Order w.r.t. $NO_2 = 2$; Overall order = 3

21. s^{-1} **22.** $\frac{1}{2}\frac{\Delta[H_2O]}{\Delta t} = \frac{\Delta[O_2]}{\Delta t}$ **23.** 9.1×10^{-2} mol^{-1} L s^{-1}

24. Flow methods, Relaxation method or spectrophotometric techniques

25. Molecularity = 2; order = 1

DESCRIPTIVE QUESTIONS

27. Rate of reaction $= -\frac{1}{2}\frac{d[X]}{dt} = -\frac{1}{3}\frac{d[Y]}{dt} = \frac{d[X_2Y_3]}{dt}$ **32.** $\frac{d[I_2]}{dt} = -\frac{1}{2}\frac{d[HI]}{dt}$

36. (*a*) Order w.r.t. NO and overall order = 2; $k = L\ mol^{-1}\ s^{-1}$

(*b*) Order w.r.t. $H_2O_2 = 1$, order w.r.t. $I^- = 1$; order w.r.t. $H^+ = 0$

Overall order = 2

$k = L\ mol^{-1}\ s^{-1}$

(*c*) Order w.r.t. CH_3CHO and overall order = 1.5

$k = L^{1/2}\ m^{-1/2}\ s^{-1}$

(*d*) Order w.r.t. $CHCl_3 = 1$; order w.r.t. $Cl_2 = 0.5$; overall order = 1.5

$k = L^{1/2}\ mol^{-1/2}\ s^{-1}$

(*e*) Order w.r.t. $C_2H_5Cl = 1$; overall order = 1

$k = s^{-1}$

42. (*a*) Rate $= k[H_2][I_2]$; (*b*) Rate $= k[H_2][I_2]$; (*c*) Rate $= k[H_2][I_2]$

46. $t_{3/4} = 2 \times t_{1/2}$; $t_{7/8} = 3 \times t_{1/2}$ **47.** $C_n = C_0 \times (1/2)^n$

59. Units of rate = atm s^{-1}; units of $k = (atm)^{-1/2}\ s^{-1}$

60. 1st order w.r.t. A and 2nd order w.r.t. B_2

74. Zero order reaction

75. $2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$. With the progress of reaction, conc. of Mn^{2+} ions increase which act as catalyst for the reaction. Consequently reaction rate increases with passage of time.

76. From the equation $k = Ae^{-E_a/RT}$. If $T \longrightarrow \infty$, $k \longrightarrow A$. Thus $E_a = 0$. This is not probable.

NUMERICAL PROBLEMS

88. Initial concentration of Y = 10.0 M. Throughout the reaction its concentration cannot fall below 9.9 M even for complete disappearance of X (0.1 M). Thus conc. of Y may be assumed constant and the rate expression would be

Rate $= 10.0 \times k[A]$

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Taking 0.6 k as another constant k', the formula can be applied for 1st order

$$k' = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$

$$10.0 \times k = \frac{2.303}{t} \log \frac{[A]_0}{[A]}$$. Substitute k, and $[A]_0$ and calculate [A]

$$[A] = \mathbf{6.7 \times 10^{-4}\ mol\,L^{-1}}$$

89. Overall reaction is $1/2\ A_2 + C \longrightarrow AC$

$$K_{eq} \text{ for 1st step} = \frac{k_f}{k_b} = \frac{10^{10}}{10^{10}} = 1$$

Rate law will be $\quad$ Rate $= (K_{eq})^{1/2} k_2 [A_2]^{1/2} [C]$

or $\quad$ Rate $= k [A_2]^{1/2} [C]$ $\quad$ [$\because$ $K_{eq} = 1$]

91. (*a*) 2nd order in NO and 1st order in Cl_2 ; (*b*) 180 $mol^{-2} L^2 s^{-1}$

92. Hydrolysis of sucrose in mineral acid proceeds as

$$\underset{\substack{\text{(Dextro-rotatory)}\\ +66.5^\circ}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{H^+} \underset{\substack{\text{Glucose}\\ \text{(Dextro-rotatory)}\\ +52.5^\circ}}{C_6H_{12}O_6} + \underset{\substack{\text{Fructose}\\ \text{(Laevo rotatory)}\\ -92.^\circ}}{C_6H_{12}O_6}$$

Laevo-rotatory

Since dextro rotatory sucrose gradually changes into laevo rotatory mixture, the reaction is called **inversion of sucrose.** The kinetics of this reaction is followed by noting the angle of rotation with the help of polarimeter

Reading at time zero $= r_0$

Reading at time 't' $= r_t$

Reading at time ∞ $= r_\infty$

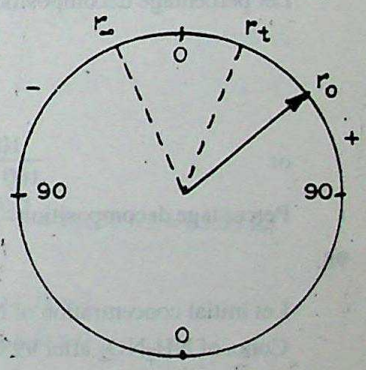

Fig. 6.16

As evident,

Amount of sucrose hydrolysed $(x) \propto (r_0 - r_t)$

Initial amount of sucrose $(a) \propto (r_0 - r_\infty)$

The formula thus, becomes $\quad k = \frac{2.303}{t} \log \frac{r_0 - r_\infty}{r_0 - r_t}$

Substitute the values of r_0, r_∞ and r_t find the value of k, it will be constant

$$k = \frac{2.303}{10} \log \frac{35.2}{33.0} = \mathbf{0.0064\ min^{-1}}$$

$$t_{1/2} = \frac{0.693}{k} = \frac{0.693}{0.0064} = \mathbf{108.3\ min}$$

93. $$k = \frac{2.303}{t} \log \frac{a}{a-x} = \frac{2.303}{55} \log \frac{0.62}{0.44} = \mathbf{6.24 \times 10^{-3}\ sec^{-1}}$$

when $\quad t = 100$ sec

$$6.24 \times 10^{-3} = \frac{2.303}{100} \log \frac{0.062}{a-x}$$

or $$\log \frac{0.062}{a-x} = \frac{6.24 \times 10^{-3} \times 100}{2.303} = 0.2709$$

or $\quad (a - x) = \mathbf{0.033\ atm}$

94. $$k = \frac{\text{Rate}}{[N_2O_5]} = \frac{1.3 \times 10^{-4}}{0.22} = \mathbf{5.91 \times 10^{-4}\ sec^{-1}}$$

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95. $$k = \frac{0.693}{14.5}\ \text{min}^{-1} = 4.78 \times 10^{-2}\ \text{min}^{-1}$$

Let decrease in pressure of CH_3OCH_3 be p atm in 12 min.

$\therefore$ $$(a - x) \propto (0.40 - p)$$

$$k = \frac{2.303}{t} \cdot \log \frac{a}{a - x}$$

$$4.78 \times 10^{-2} = \frac{2.303}{12} \log \left(\frac{0.40}{0.4 - p} \right) \text{ solve for } p$$

or $$p = \mathbf{0.1745\ atm}$$

97. Calculate of k_{25}

$$k_{25} = \frac{2.303}{t} \log \frac{a}{a - x} = \frac{2.303}{20} \log \frac{a}{a - 0.25a}$$

$$= \frac{2.303}{20} \log \frac{1}{0.75} = \mathbf{0.01439\ min^{-1}}$$

Now, $$\log k_{40}/k_{25} = \frac{E_a}{2.303\ R} \left[\frac{T_2 - T_1}{T_1 T_2} \right] = \frac{70000}{2.303 \times 8.314} \left[\frac{313 - 298}{313 \times 298} \right] = 0.5879$$

$$\frac{k_{40}}{0.01439} = \text{antilog } 0.5879 = 3.872$$

$$k_{40} = 3.872 \times 0.01439 = \mathbf{0.0557\ min^{-1}}$$

% decomposition,

Let percentage decomposition be x

$\therefore$ $$a = 100,\ a - x = (100 - x)$$

$$k_{40} = \frac{2.303}{20} \cdot \log \frac{100}{100 - x} \text{ or } \log \frac{100}{100 - x} = \frac{0.0557 \times 20}{2.303}$$

or $$\frac{100}{100 - x} = 3.045 \quad \text{or} \quad x = 67.16$$

Percentage decomposition $= 67.16\%$

98. $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{2.1} = 0.33\ \text{hr}^{-1}$$

Let initial concentration of $NH_2NO_2 = 100$

Conc. of NH_2NO_2 after 99% decomposition $= 100 - 99 = 1$

$\therefore$ $$t = \frac{0.693}{k} \log \frac{a}{a - x} = \frac{0.693}{0.33} \log \frac{100}{1} = \mathbf{13.96\ hr}$$

Mol. mass of NH_2NO_2 $= 62$

$\therefore$ Moles of NH_2NO_2 decomposed $= \dfrac{6.2 \times 99}{62 \times 100} = 0.099$

1 mole of NH_2NO_2 gives N_2O $= 22.4$ L at N.T.P.

0.099 mol of NH_2NO_2 gives N_2O $= 0.099 \times 22.4 = \mathbf{2.217\ L}$

99. (*i*) From the given data, the rate law comes out to be

$$R = k_1 [A]^2 [B] \qquad \therefore \quad \text{Order w.r.t. A} = 2$$

Order w.r.t. B = 1

(*ii*) Now $$k_1 = \frac{\text{Rate}}{[A]^2 [B]} = \frac{5.0 \times 10^{-4}}{(2.5 \times 10^{-4})^2 (3 \times 10^{-5})} = \mathbf{2.67 \times 10^8\ L^2\ mol^{-2}\ s^{-1}}$$

(*iii*) $$k_2 = \frac{2.0 \times 10^{-3}}{(2.5 \times 10^{-4})^2 (3.0 \times 10^{-5})} = \mathbf{1.07 \times 10^9\ L^2\ mol^{-2}\ s^{-1}}$$

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$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times 8.314}\left[\frac{T_2 - T_1}{T_1T_2}\right]$$

or $$\log \frac{1.07 \times 10^9}{2.69 \times 10^8} = \frac{E_a}{2.303 \times 8.314}\left[\frac{320 - 300}{320 \times 300}\right] \text{ or } E_a = 5.53 \times 10^4 \text{ J}$$

or $$E = \mathbf{55.3\ kJ}$$

(*iv*) **Calculation of A** $$k = A.e^{-E_a/RT}$$

$$\log k = \log A - \frac{E_a}{2.303\ R}$$

$$\log A = \log (2.67 \times 10^8) - \frac{5.53 \times 10^4}{2.303 \times 8.314 \times 300} = 18.0565$$

or $$A = \mathbf{1.145 \times 10^{18}}.$$

100. (*i*) 'At equilibrium, the conc. of A falls from 0.6 mol L^{-1} to 0.3 mol L^{-1} and conc. of B rises from zero to 0.6 mol L^{-1}. Thus, 0.3 mol L^{-1} of A on decomposition gives 0.6 mol L^{-1} of B

$\therefore$ $$\mathbf{n = 2}$$

(*ii*) $$K = \frac{[B]^2}{[A]} = \frac{(0.6)^2}{0.3} = \mathbf{1.2}$$

(*iii*) Initial rate of conversion of A $$= -\frac{\Delta[A]}{\Delta t} = -\frac{0.5 - 0.6}{1}$$

$$= \frac{0.1}{1} = \mathbf{0.1\ mol\ L^{-1}\ hr^{-1}}$$

101. $$\log \frac{k_2}{k_1} = \frac{E_a}{2.303 \times R}\left[\frac{410 - 350}{410 \times 350}\right]$$

$$\log 6 = \frac{E_a}{2.303 \times 8.314} \times \frac{60}{410 \times 350}$$

or $$E_a = \frac{0.7782 \times 2.303 \times 8.314 \times 410 \times 350}{60} = 35636.6\ \text{J} = \mathbf{35.63\ kJ}$$

102. (*i*) From the data of initial rates, the rate is

$$\text{rate} = k\,[A]^2[B]^0 \qquad \therefore \text{ Order w.r.t. A} = 2$$

Order w.r.t. B = 0

(*ii*) $$4.0 \times 10^{-4} = k[0.1]^2[0.1]^0$$

or $$k = \frac{4.0 \times 10^{-4}}{0.1 \times 0.1} = \mathbf{4 \times 10^{-2}\ L\ mol^{-1}s^{-1}}$$

(*iii*) $$\text{Rate} = k\,[0.2]^2[0.35]^0$$

$$= 4 \times 10^{-2} \times 0.2 \times 0.2 = \mathbf{1.6 \times 10^{-3}\ mol\ L^{-1}\ s^{-1}}$$

103. $$k_1 = \frac{0.693}{360} = 1.92 \times 10^{-3}\ \text{min}^{-1}$$

$$\log \frac{k_2}{k_1} = \frac{E_a}{2.303\ R}\left[\frac{T_2 - T_1}{T_1T_2}\right] = \frac{200 \times 10^3}{2.303 \times 8.314}\left[\frac{723 - 653}{653 \times 723}\right]$$

$$= \frac{200 \times 10^3 \times 70}{2.303 \times 8.314 \times 653 \times 723} = 1.5487$$

$$\frac{k_2}{k_1} = \text{Antilog}\,(1.5487) = 35.38$$

$$k_2 = 35.38 \times 1.92 \times 10^{-3} = 6.792 \times 10^{-2}\ \text{min}^{-1}$$

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Rate at 450°

$$t = \frac{2.303}{k_2}\log\frac{100}{100-75} = \frac{2.303}{6.792\times10^{-3}}\log\frac{100}{25}$$

$$= \frac{2.303\times0.6021}{6.792\times10^{2}} = \mathbf{20.415\ min.}$$

104. $$NH_4^+ + aq \rightleftharpoons NH_3 + H^+ ;\ K = \frac{[NH_3][H^+]}{[NH_4^+]} = 5.6\times10^{-10}\ \text{(given)} \quad ...(i)$$

Also, $$NH_4^+ + OH^- \underset{k_b}{\overset{k_f}{\rightleftharpoons}} NH_3 + H_2O ;\ k_f = 3.4\times10^{10}\ L\ mol^{-1}\ \text{(given)}$$

The equilibrium is to determine rate constant k_b for backward reaction, *i.e.*, $NH_3 + H_2O \longrightarrow NH_4^+ + OH^-$

Now, the equilibrium constant for the above equilibrium k'

$$k' = \frac{k_f}{k_b} = \frac{[NH_3][H_2O]}{[NH_4^+][OH^-]} = \frac{[NH_3]}{[NH_4^+][OH^-]}$$

or $$\frac{k_f}{k_b} = \frac{K}{[H^+][OH^-]} \qquad \left[\because \text{ From } (i),\ \frac{[NH_3]}{[NH_4^+]} = \frac{k}{[H^+]}\right]$$

$\therefore$ $$k_b = \frac{k_f[H^+][OH^-]}{K} = \frac{3.4\times10^{10}\times1\times10^{-14}}{5.6\times10^{-10}} = \mathbf{6.07\times10^{5}\ s^{-1}}$$

105. Given that $$\log k = 14.34 - \frac{1.25\times10^4}{T} \quad ...(i)$$

Also according to Arrhenius equation

$$k = Ae^{-E_a/RT}$$

or $$\ln = \frac{k}{A} = -\frac{E_a}{RT} \quad \text{or} \quad \log k = \log A - \frac{E_a}{2.303\ RT} \quad ...(ii)$$

Comparing equation (*i*) and (*ii*), we have

$$\frac{E_a}{2.303\ RT} = \frac{1.25\times10^4}{T} \quad \text{or} \quad E_a = 1.25\times10^4\times2.303\times R$$

$$= 1.25\times10^4\times2.303\times8.314\ J\ mol^{-1}$$

$$= \mathbf{239.3\ kJ\ mol^{-1}}$$

Now $$k = \frac{0.693}{t_{1/2}} = \frac{0.693}{256}\ min^{-1}$$

Substitute in (*i*), we have

$$\log\frac{0.693}{256} = 14.34 - \frac{1.25\times10^4}{T}$$

or $$-2.56 = 14.34 - \frac{1.25\times10^4}{T} \quad \text{or} \quad \mathbf{T = 739.6\ K}$$

106. Rate = $k[A]^2[B]^0$, Overall order = **2.** Order w.r.t. A = **2**, order w.r.t. B = **0.**

MULTIPLE CHOICE QUESTIONS

1. (*b*)	**2.** (*a*)	**3.** (*a*)	**4.** (*a*)	**5.** (*b*)	**6.** (*b*)
7. (*c*)	**8.** (*b*)	**9.** (*d*)	**10.** (*d*)	**11.** (*b*)	**12.** (*a*)
13. (*c*)	**14.** (*d*)	**15.** (*b*)	**16.** (*c*)	**17.** (*a*)	**18.** (*d*)

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19. (*d*)	**20.** (*c*)	**21.** (*a*)	**22.** (*c*)	**23.** (*b*)	**24.** (*b*)
25. (*a*)	**26.** (*c*)	**27.** (*c*)	**28.** (*d*)	**29.** (*d*)	**30.** (*b*), (*c*)
31. (*b*)	**32.** (*a*)	**33.** (*b*)	**34.** (*c*)	**35.** (*d*)	**36.** (*b*)
37. (*b*)	**38.** (*a*)	**39.** (*d*)	**40.** (*b*).		

FILL IN THE BLANKS

1. Pseudo, first	**2.** Faster	**3.** Photochemical
4. Slowest	**5.** Order	**6.** 0.693/*k*
7. 0.5	**8.** May or may not	**9.** visible radiations
10. atm sec^{-1}	**11.** k_{308}/k_{298}	**12.** *k*
13. Cannot	**14.** Three	**15.** $-\Delta[B]/\Delta t$
16. At $T \longrightarrow \infty$		

TRUE/FALSE STATEMENTS

1. True	**2.** False	**3.** False	**4.** True	**5.** False	**6.** False
7. True	**8.** False	**9.** False	**10.** True	**11.** True	**12.** False
13. True	**15.** True.				

MATCHING TYPE QUESTIONS

1—3—5 ; 2—1—4 ; 3—5—1 ; 4—2—3 ; 5—4—2.

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7A

Nomenclature of Organic Compounds

The term nomenclature means the system of naming of organic compounds. In the early stages of development of organic chemistry, the organic compounds were named after the source from which they were prepared. For example, the name *acetic acid* was derived from *acetum* (Latin : *acetum* means vinegar). Similarly, the name *formic acid* was derived from *formicus* (means *red ants*) because the compound was obtained by the distillation of red ants. Methyl alcohol was named *wood-spirit* as it was obtained from the destructive distillation of wood. These names of organic compounds are called **common names** or **trivial names.** The common names were assigned to the organic compounds at the whim and fancy of the discoverer and there was no systematic basis. In many cases, even the same compound was given more than one names. For example, methane was named as *marsh gas* as well as *damp fire*.

Towards the end of nineteenth century the number of organic compounds known was so large that it became difficult to remember individual names of the organic compounds. In order to rationalise the system of nomenclature, an international congress of chemists was held in Geneva in 1892. It led to the development of comprehensive system of nomenclature known as *Geneva system*. There was further improvement in Geneva system in 1931 by *International Union of Chemists*. This improved system is referred to as **IUC System.**

The IUC system has been further revised by the International Union of Pure and Applied Chemistry in the light of practical difficulties. This revised system of nomenclature has been accepted all over the world and is abbreviated as **IUPAC system** of nomenclature.

NOMENCLATURE OF ALIPHATIC COMPOUNDS

According to IUPAC system, the name of organic compound, in general, consists of the following parts.

(*i*) *Word root* (*ii*) *Primary suffix* (*iii*) *Secondary suffix* (*iv*) *Prefix*

(*i*) **Word root.** The word root represents the number of carbon atoms in the *parent chain*. The parent chain in the compound is selected by following certain rules as discussed in **Rule 1.** For the chains upto four carbon atoms special word roots are used, but for the chains containing more than four carbon atoms, Greek numerals are used. The general word root for different aliphatic compounds is **ALK.** The word roots for different lengths of carbon chains are given below in Table 1.

Table 1. Word Roots for different lengths of Carbon Chains

Chain Length	*Word root*	*Chain Length*	*Word root*
C_1	Meth-	C_9	Non-
C_2	Eth-	C_{10}	Dec-
C_3	Prop-	C_{11}	Undec-
C_4	But-	C_{12}	Dodec-
C_5	Pent-	C_{13}	Tridec-
C_6	Hex-	C_{18}	Octadec-
C_7	Hept-	C_{20}	Icos-
C_8	Oct-	C_{30}	Tricont-

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(*ii*) **Primary Suffix.** Primary suffix is used to represent saturation or unsaturation in the carbon chain. While writing the name, primary suffix is added to the word root. Some of the primary suffixes are given below in Table 2.

Table 2. Some Primary Suffixes

Nature of Carbon Chain	*Primary Suffix*
Saturated Carbon Chain	*ane*
Unsaturated Carbon Chains :	
one C = C bond	*ene*
two C = C bonds	*adiene*
three C = C bonds	*atriene*
one C ≡ C bond	*yne*
two C ≡ C bonds	*adiyne*

(*iii*) **Secondary Suffix.** Secondary suffix is used to indicate the functional group in the organic compound. It is added to the primary suffix by dropping its terminal **e**. Secondary suffixes for various functional groups are given in Table 3.

Table 3. Some Organic Families and Secondary Suffixes

Class of organic compound	*General formula*	*Functional Group*	*Suffix*	*IUPAC name of the family* (*Word root* + *p suffix* + *sec. suffix*)
Alcohols	R—OH	—OH	-ol	ALKANOL
Thioalcohols	R—SH	—SH	-thiol	ALKANETHIOL*
Amines	R—NH_2	—NH_2	-amine	ALKANAMINE
Aldehydes	R—CHO	—CHO	-al	ALKANAL
Ketones	R—COR	>CO	-one	ALKANONE
Carboxylic acids	R—COOH	—COOH	-oic acid	ALKANOIC ACID
Amides	R—$CONH_2$	—$CONH_2$	-amide	ALKANAMIDE
Acid chlorides	R—COCl	—COCl	-oyl chloride	ALKANOYL CHLORIDE
Esters	R—COOR	—COOR	-oate	ALKYL ALKANOATE
Nitriles	R—C ≡ N	—C ≡ N	-nitrile	ALKANE NITRILE*

***Note.** (*a*) *If the name of the secondary suffix begins with a consonent, then the terminal 'e' of the primary suffix is not dropped while adding secondary suffix to it.*

(*b*) *The terminal 'e' of primary suffix is also retained if some numerical prefix like di, tri, etc., is used before the secondary suffix.*

(*iv*) **Prefix.** Prefix is a part of the name which appears before the word root. Prefixes are used to represent the names of alkyl groups (branched chains) or some functional groups which are regarded as substituents as described below :

(*a*) **Alkyl groups** are formed by the removal of H atom from the alkanes. These are represented by the general formula C_nH_{2n+1}- or R-. Some alkyl groups along with their prefixes are given in Table 4.

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Table 4. Some Alkyl Groups along with their Prefixes

Alkane	*Alkyl Group*	*Abbreviation*	*Prefix*
CH_4	CH_3—	Me-	Methyl
C_2H_6	CH_3CH_2—	Et-	Ethyl
C_3H_8	$CH_3CH_2CH_2$—	*n*-Pr-	*n*-Propyl
C_3H_8	CH_3—CH(—CH_3)—	Iso-Pr-	Isopropyl or (1-Methyl ethyl)

(*b*) **Some functional groups** are always indicated by the prefixes instead of secondary suffixes. These functional groups along with their prefixes are listed below in Table 5.

Table 5. Functional groups which are always represented by prefixes

Functional Group	*Prefix*	*Family*	*IUPAC Name*
—NO_2	Nitro	R—NO_2	NITROALKANE
—OR′	alkoxy	R—OR′	ALKOXYALKANE
—Cl	Chloro	R—Cl	CHLOROALKANE
—Br	Bromo	R—Br	BROMOALKANE
—I	Iodo	R—I	IODOALKANE
—F	Fluoro	R—F	FLUOROALKANE
—NO	Nitroso	R—NO	NITROSOALKANE

(*c*) **In poly functional compounds,** *i.e.*, compounds with more than one functional groups, one of the functional groups is treated as principal functional group and is indicated by the secondary suffix whereas other functional groups are treated as substituents and are indicated by the prefixes. The order of priority among various functional groups to be treated as principal functional group has been discussed in *Section D*. The prefixes for various functional groups are given in Table 6.

Table 6. Prefixes for functional groups in polyfunctional compounds

Functional Group	*Prefix*
—OH	Hydroxy
—CN	Cyano
—NC	Isocyano
—CHO	Formyl or Aldo
—SH	Mercapto
—SR	Alkylthio
—COOH	Carboxy
—COOR	Carbalkoxy
—COCl	Chloroformyl
—$CONH_2$	Carbamoyl
—NH_2	Amino
= NH	Imino
>CO	Keto or Oxo

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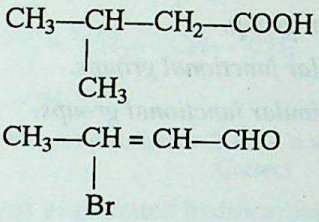
Arrangement of Prefixes, Word root and Suffixes. The prefixes, word root and suffixes are arranged as follows while writing the name

Prefix(es) + Word root + p. suffix + sec. suffix

The above arrangement is illustrated by the following examples.



Methyl.....but.....an.....oicacid			
prefix	word root	primary suffix	secondary suffix

Bromo.....but.....en.....al			
prefix	word root	primary suffix	secondary suffix

Some Important Points

Note 1. *The name of organic compound may or may not contain prefix or secondary suffix but it always contains word root and primary suffix. For example, the names of straight chain alkanes, alkenes and alkynes do not contain any prefix and secondary suffix.*

$CH_3CH_2CH_2CH_2CH_3$

Pent.....ane	
word root	primary suffix

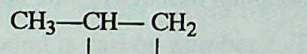
$CH_3CH = CHCH_3$

But.....ene	
word root	primary suffix

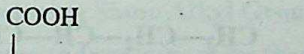
2. *Numerical prefixes such as* **di, tri,** *etc., are used before the prefixes or secondary suffixes, if the compound contains more than one similar substituents or similar functional groups.*

Di.....methyl.....but.....an.....oic acid				
Numerical Prefix	prefix	word root	p. suffix	sec. suffix

While adding numerical prefix before the secondary suffix, the terminal 'e' of the primary suffix is retained.

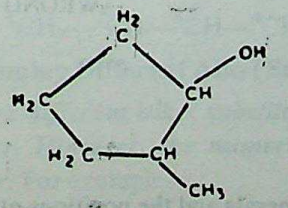


Prop.....ane.....di.....ol			
word root	p. suffix	Numerical prefix	sec. suffix



Eth.....ane.....di.....oic acid			
word root	p. suffix	Numerical prefix	sec. suffix

3. *In case of* **alicyclic compounds,** *a separate secondary prefix cyclo is used immediately before the word root. Word root, here depends upon the number of carbon atoms in the ring.*



Methyl.....cyclo.....pent.....an.....ol				
prefix	sec. prefix	word root	p. suffix	sec. suffix

4. *Besides arranging various prefixes, word root and suffixes, the positions of substituents, multiple bonds and functional groups in the compound are indicated by Arabic numerals. The numbering of carbon atoms of the parent chain is done as discussed in* **Rule 2.**

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VARIOUS RULES FOR WRITING IUPAC NAMES

In order to have better understanding of various rules of nomenclature, let us discuss it in different parts as described below :

(A) *Nomenclature of hydrocarbons.*

(B) *Nomenclature of compounds containing one functional group.*

(C) *Nomenclature of compounds with more than one similar functional groups.*

(D) *Nomenclature of compounds with more than one dissimilar functional groups.*

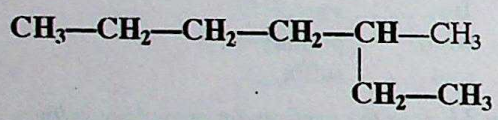
(E) *Nomenclature of alicyclic compounds.*

(A) NOMENCLATURE OF HYDROCARBONS

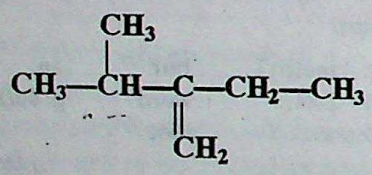
Hydrocarbons are named according to the following general rules :

Rule 1. Longest Chain Rule

Select the longest continuous chain of carbon atoms as the parent chain. If some carbon-carbon multiple bond is present, the parent chain must contain the carbon atoms involved in it. The number of carbon atoms in the parent chain determines the *word root.* The carbon atoms which are not included in the parent chain are considered as alkyl substituents and determine the *prefixes.*

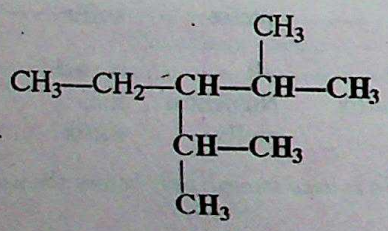


Prefix : *methyl*
Word root : *hept*
p. suffix : *ane*



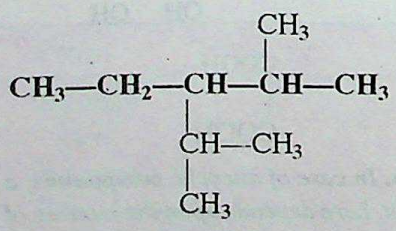
Prefixes : *ethyl ; methyl*
Word root : *but*
p. suffix : *ane*

If two equally long chains are possible, the chain with maximum number of side chains is selected as parent chain. For example,



CORRECT

Prefixes : *ethyl ; dimethyl*
word root : *pent*
p. suffix : *ane*



WRONG

Rule 2. Lowest Number or Lowest Sum Rule

The selected parent chain is numbered using Arabic numerals and the positions of the alkyl groups are indicated by the number of the carbon atom to which the alkyl group is attached. ***The numbering is done in such a way that the substituted carbon atoms have the lowest possible numbers.*** In other words, ***the sum of the numbers used to indicate the positions of various alkyl groups must be lowest.*** Some examples are given below :

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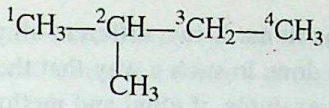
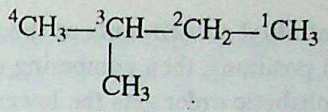
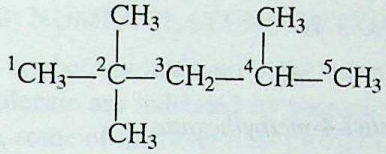
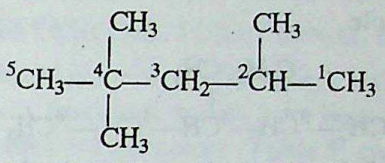
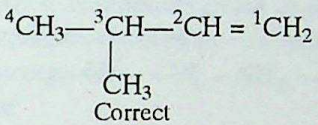

Correct

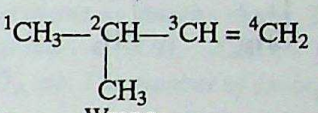

Wrong


Sum of positions = 2 + 2 + 4 = 8
Correct


Sum of positions = 2 + 4 + 4 = 10
Wrong

In case of unsaturated hydrocarbons, the carbon atoms involved in the multiple bond should get the lowest possible number. For example,

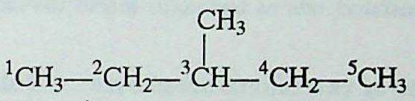

Correct


Wrong

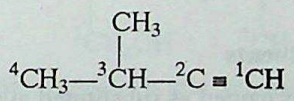
The name of the compound, in general, is written in the following sequence :

(*Position of substituents*)—(*Prefixes*) (*Word root*) (*p. suffix*)

The above sequence is illustrated in the following examples



Here, prefix is *methyl* ; the methyl group is at carbon number *3* in the parent chain. Word root is *pent* and primary suffix is *ane*. Hence, the name is : ***3-Methylpentane***

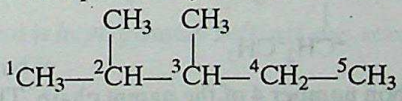


Here, prefix is *methyl* ; Word root is *but* ; primary suffix is *yne*. Methyl group is at the carbon number *3* and the triple bond is carbon number *1*. Thus, the name is :

3-Methyl-1-butyne.

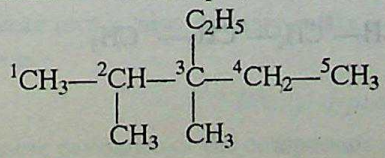
Rule 3. Naming Same Alkyl Groups at Different Positions

If the compound contains more than one similar alkyl groups, their positions are indicated separately and an appropriate numerical prefix : di, tri, etc., is attached to the name of the substituent. The positions of the substituents are separated by commas. For example,


2,3-Dimethylpentane

Rule 4. Naming Different Alkyl Substituents

If there are different alkyl substituents present in the compound, their names are written in the alphabetical order. However, the numerical prefixes such as di, tri, etc., are not considered for the alphabetical order. For example,


3-Ethyl-2,3-dimethylpentane

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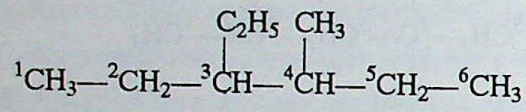
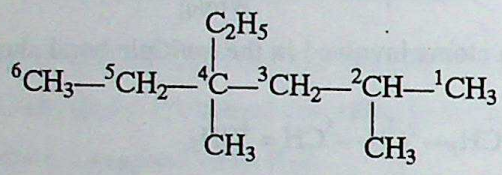
Naming different alkyl substituents at the equivalent positions. If two different alkyl groups are located at the equivalent positions, then numbering of the chain is done in such a way that the alkyl group which comes first in alphabetic order gets the lower position. For example, if ethyl and methyl groups are present at equivalent positions, then carbon bearing ethyl group should get the lower number as illustrated in the following example.

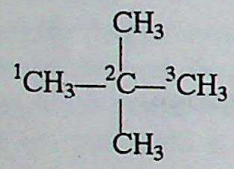


3-Ethyl-4-methylhexane

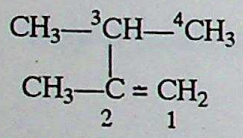
In the light of the above rules, let us write the IUPAC names of some aliphatic hydrocarbons.



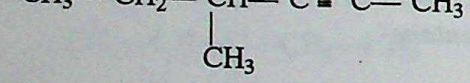
4-Ethyl-2,4-dimethylhexane



2,2-Dimethylpropane



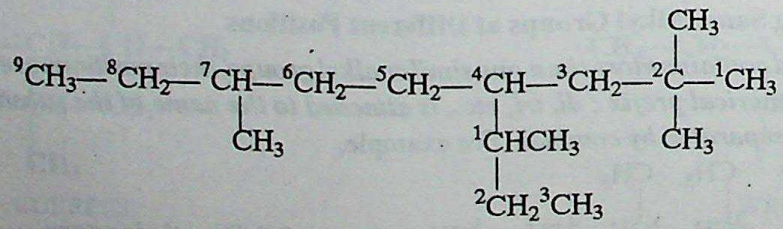
2, 3-Dimethyl-1-butene



4-Methyl-2-hexyne

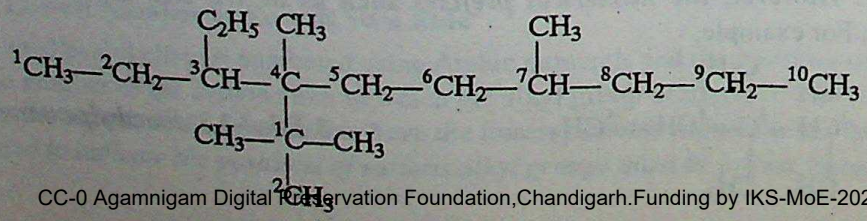
Rule 5. Naming the Complex Alkyl Substituents

If the alkyl substituent is further branched it is named as substituted alkyl group. For this purpose, the carbon atoms of the alkyl group are separately numbered in such a way, that the carbon atom directly attached to the parent chain is given number 1. The prefix/name of such a substituent is enclosed in brackets as illustrated in the following examples.



Here, substituted propyl group is present at carbon number 4 of the parent chain. The propyl group has methyl substituent at carbon number 1 of the alkyl group. Thus, the name of the above compound is :

2, 2, 7-Trimethyl-4-(1-methyl propyl) nonane



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Here, substituted ethyl group is present at carbon number 4 of the parent chain. The ethyl group has two methyl substituents as carbon 1 of the alkyl group. Thus, the name of the compound is,

3-Ethyl-4-(1,1-dimethtyl ethyl)-4,7-dimethyldecane.

(B) NOMENCLATURE OF COMPOUNDS HAVING ONE FUNCTIONAL GROUP

It has been pointed out in the beginning that the functional groups (other than C = C or C ≡ C) present in the molecule are indicated by secondary suffixes. Such functional groups have been listed in **Table 3.** However, some of the functional groups are always regarded as substituents (**Table 5**) and are indicated by the prefixes. The various, rules which are followed while writing the name of the compounds having one functional group are described below.

Rule 1. Longest chain rule

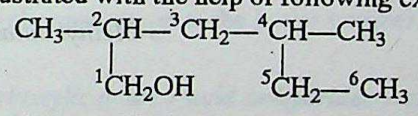
Select the longest continuous chain of the carbon atoms as **parent chain.** *The selected chain must include the carbon atoms involved in the functional groups like —COOH, —CHO, —CN, etc., or those which carry the functional groups like —OH, —NH_2, —Cl, —NO_2, etc. The number of carbon atoms in parent chain decides the word root.*

Rule 2. Lowest number rule

The carbon atoms of the parent chain are numbered in such a way so that the carbon atom of the functional group gets the lowest possible number. In case the functional group does not have the carbon atom, then the carbon atom of the parent chain attached to the functional group should get the lowest possible number.

Rule 3, Rule 4 and **Rule 5** are used in the similar way as described in case of hydrocarbons earlier.

The above rules are illustrated with the help of following examples.



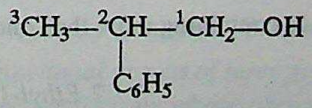
Here, word root is *hex*, primary suffix is *ane*, secondary suffix is *ol* and prefix is *methyl*. The two methyl groups are located at position 2 and 4 in the parent chain.

Arranging the prefixes, word root and suffixes in proper order along with their respective positions, the name of the above compound is

2, 4-Dimethyl-1-hexanol or *2, 4-Dimethyl hexan-1-ol*

Here, word root is *hept*, primary suffix is *ene*, secondary suffix is *al* and prefix is *ethyl*. Thus, the name of the above compound is

5-Ethyl-3-heptenal



Here, word root is *prop*, primary suffix is *ane*, secondary suffix is *ol* and prefix is *phenyl* (for C_6H_5—). Thus, the name is :

2-Phenyl-1-propanol

Some more examples of the compounds containing one functional group are being given below.

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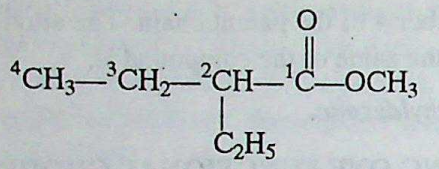
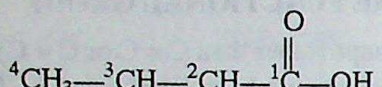
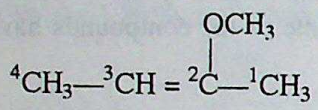


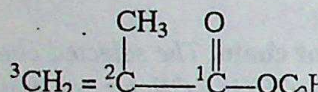
Methyl 2-ethylbutanoate



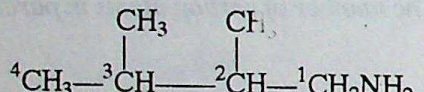
But-2-en-1-oic acid or *2-Butenoic acid*



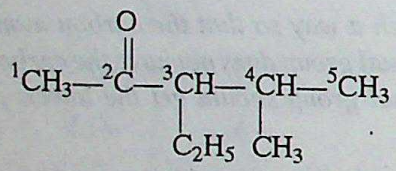
2-Methoxy-2-butene



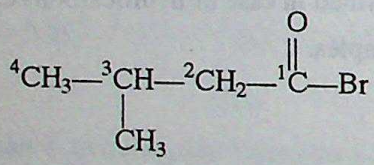
Ethyl 2-methylprop-2-enoate



2, 3-Dimethyl-1-butanamine



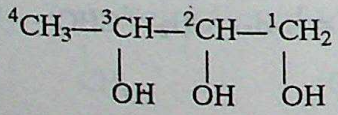
3-Ethyl-4-methyl-2-pentanone



3-Methyl butanoyl bromide

C. NAMING THE COMPOUNDS WITH MORE THAN ONE SIMILAR FUNCTIONAL GROUPS

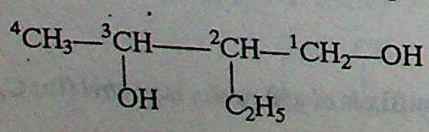
If the organic molecule contains more than one similar functional groups, then in addition to various rules, the numerical prefixes *di* (for 2), *tri* (for 3), etc., are added before the secondary suffix which indicates the functional group. While adding such words, the vowel *e* of the primary suffix is retained. For example



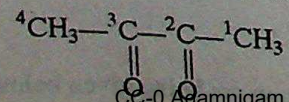
Here, word root is *but*, primary suffix is *ane* and secondary suffix is *ol*. The —OH groups are positioned at carbon number 1, 2 and 3. Thus, the name is :

1, 2, 3-Butanetriol.

Some more examples of the compounds containing more than one similar functional groups are given below.



2-Ethyl-1, 3-butanediol



2, 3-Butanedione

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$^4CH_2 = {}^3CH—{}^2CH = {}^1CH_2$ — *1, 3-Butadiene*

$$\begin{array}{l} {}^4CH_2—{}^3CH_2—{}^2CH_2 \\ \quad\;\; | \qquad\qquad\quad | \\ {}^5COOH \qquad\quad {}^1COOH \end{array}$$ — *1, 5-Pentanedioic acid*

$$\begin{array}{l} {}^4CH_2—{}^3CH = {}^2CH—{}^1CHO \\ \quad\;\; | \\ {}^5CHO \end{array}$$ — *Pent-2-ene-1, 5-dial*

$$\begin{array}{l} {}^2CH_2—{}^1CN \\ \quad\;\; | \\ {}^3CH_2—{}^4CN \end{array}$$ — *1, 4-Butanedinitrile*

$$\begin{array}{l} {}^1CH_2—{}^2CH—{}^3CH_2—{}^4CH_2 \\ \quad\;\; | \qquad\;\; | \qquad\qquad\quad | \\ NH_2 \quad CH_3 \qquad\qquad NH_2 \end{array}$$ — *2-Methyl-1, 4-butanediamine*

$$\begin{array}{l} \qquad\quad CH_2Cl \\ \qquad\quad\;\; | \\ {}^3CH_2—{}^2CH—{}^1CH_2 \\ \quad\;\; | \qquad\qquad\quad | \\ \quad Cl \qquad\qquad\quad Cl \end{array}$$ — *1, 3-Dichloro-2-(chloromethyl) propane*

(D) NAMING THE COMPOUNDS WITH TWO OR MORE DIFFERENT FUNCTIONAL GROUPS

If the molecule contains more than one dissimilar functional groups, the parent chain must contain maximum possible number of functional groups. The numbering of the parent chain is done in such a way so that the functional group of higher priority gets the lower number. **The order of priority** of various groups for the sake of numbering is :

Sulphonic acids > Carboxylic acids > acid anhydrides > esters > acidchlorides > amides > nitriles > aldehydes > ketones > alcohols > amines > alkenes, alkynes > halo, nitro, alkoxy > alkyl.

As pointed out earlier, that the functional group which gets priority is treated as **principal functional group** and is indicated by the secondary suffix. On the other hand, the other functional groups in the compound are considered as substituents and are indicated by suitable prefixes. The prefixes for such functional groups have been given in **Table 6.** Let us write the IUPAC name of the following poly-functional compound.

$$\begin{array}{l} \qquad\quad CH_3 \\ \qquad\quad | \\ {}^4CH_3—{}^3C——{}^2C—{}^1CH_3 \\ \qquad\quad | \qquad\;\; \| \\ \qquad\quad OH \qquad\; O \end{array}$$

Here, the word root is *but*, and primary suffix is *one*. There are two functional groups but *CO* group gets preference over —OH group. Thus, secondary suffix is *one*. The prefixes are, *methyl* and *hydroxy*. Thus, the name is :

3-Hydroxy-3-methyl-2-butanone

It may be noted that if two functional groups of same preference appear at identical positions from the either end of the chain, then the functional group whose prefix comes first in alphabetic order gets the lower number. For example,

$$Br—{}^1CH_2—{}^2CH_2—{}^3CH_2—{}^4CH_2—{}^5CH_2—I$$

Here, *bromo* group gets preference over *iodo* group. Thus, the name of the compound is :

1-Bromo-5-iodopentane

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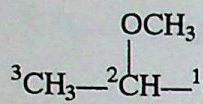
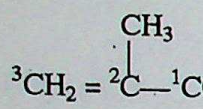
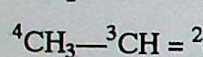
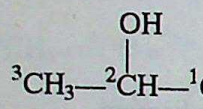
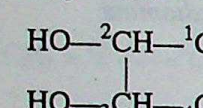
Some more examples of the poly functional compounds are given below :

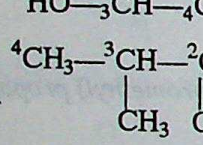

2-Methoxy propanal

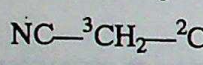

Methyl 2-methyl prop-2-enoate

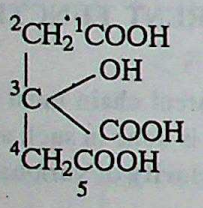

2-Butenoic acid

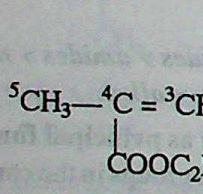

2-Hydroxy propanoic acid

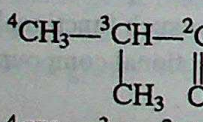

2, 3-Dihydroxy-1, 4-butanedioic acid

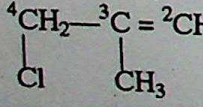

3-Methyl-2-oxobutanoic acid

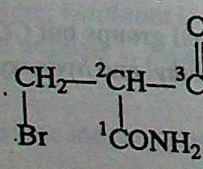

3-Cyanopropanoic acid


3-Carboxy-3-hydroxy-1, 5-pentanedioic acid


4-Carbethoxypent-3-enoic acid


2-Keto-3-methyl-(N-bromo) butanamide


4-Chloro-3-methyl-but-2-en-1-ol


2-(Bromomethyl)-3-oxopentanamide

REVIEW PROBLEMS

7.1. Write correct IUPAC names of the following poly functional compounds :

(*i*) $CH_2 = CH—CH_2Cl$ (*ii*) $CH_3CH(OH)CH(OH)CH_2OH$

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(*iii*) $(CH_3)_2CH-C(OCH_3)(CH_3)CHO$

(*iv*) $CH_3-CH(CH_2CHO)-COOH$

(*v*) $CH_3-C(CHO)(CH_2OH)-CH_2CH_3$

(*vi*) $CH_3-C(=O)-C(=O)-OCH_2CH_3$

(*vii*) $CH_3-C(=O)-C(=O)-CH_2OCH_3$

(*viii*) $H-C(=O)-C(=O)-OH$

(*ix*) $CH_3CH_2N(Cl)-C(=O)-H$

(*x*) $CH_3CH_2CH(CN)CH_2CN.$

7.2. Write IUPAC names of the following compounds :

(*i*) $CH_3OCH_2CH_2CH_2OC_2H_5$

(*ii*) $HOCH_2CH(NH_2)CHO$

(*iii*) $CH_3-C(=O)-N(H)-CH_2CH_3$

(*iv*) $HC\equiv C-CH=CH-CH_3$

(*v*) $CH_3-C(OH)(H)-COOH.$

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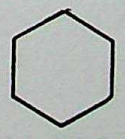
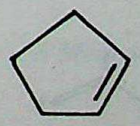
(E) NAMING OF ALICYCLIC COMPOUNDS

Names of alicyclic compounds are derived by putting another prefix '*cyclo*' before the word root which depends upon the number of carbon atoms in the ring. The suffixes *ane, ene* or *yne* are written depending upon saturation or unsaturation in the ring.



CYCLOHEXANE



CYCLOPENTENE

If some substituent or functional group is present, it is indicated by some appropriate prefix or suffix and its position is indicated by numbering the carbon atoms of the ring. *The numbering is done in such a way so as to assign least possible number to the functional group or substituent in accordance with the rules already discussed.* Some examples are :

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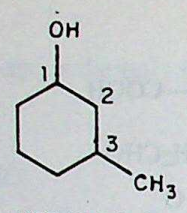
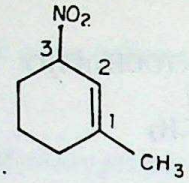
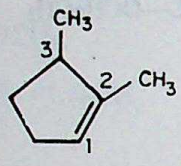


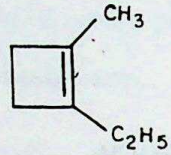
3-METHYLCYCLO-HEXANOL



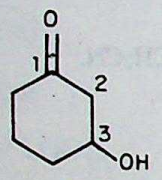
1-METHYL-3-NITROCYCLOHEXENE



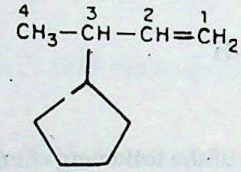
2, 3-DIMETHYLCYCLO-PENTENE



1-ETHYL-2-METHYLCYCLOBUTENE



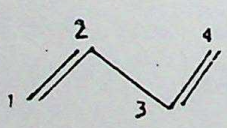
3-HYDROXYCYCLO HEXANONE



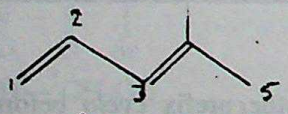
3-CYCLOPENTYL-1-BUTENE

BOND LINE NOTATIONS OF ORGANIC MOLECULES

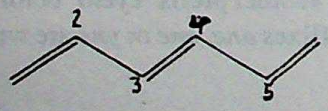
It is a simple, brief and convenient method of representing organic molecules. In these notations, the bonds between the carbon atoms are represented by lines. A single line (–) represents a single bond, two parallel lines (=) represent a double bond and three parallel lines (≡) represent a triple bond. The intersection of lines represents carbon atoms carrying appropriate number of H atoms. For example, 1, 3-butadiene ($CH_2 = CH—CH = CH_2$) can be represented as follows :



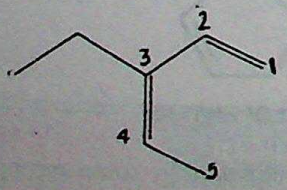
Some bond line structures along with their IUPAC names are given below :



4-Methyl-1, 3-pentadiene



1, 3, 5-Hexatriene



3-Ethyl-1, 3-pentadiene

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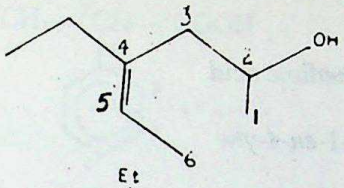
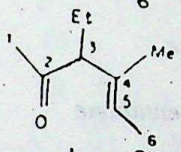
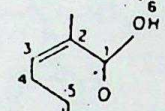


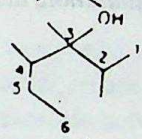
4-Ethyl-hex-4-en-2-ol



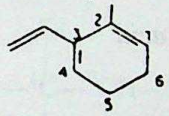
3-Ethyl-4-methylhex-4-en-2-one



2, 6-Dimethyl-2, 5-heptadienoic acid



2, 3, 4-Trimethyl-3-hexanol



3-Ethenyl-2-methyl-1, 3-cyclohexadiene

IUPAC NAMES OF SOME ORGANIC MOLECULES

$^{6}CH_3—^{5}CH_2—^{4}CH(Cl)—^{3}CH_2—^{2}CH(^{1}CH_3)—Cl$ — *2, 4-Dichlorohexane*

$^{7}CH_3{}^{6}CH(CH_3)^{5}CH_2{}^{4}CH = {}^{3}CH^{2}CH_2{}^{1}CHO$ — *6-Methylhept-3-enal*

$^{5}CH_3—^{4}C(=O)—^{3}CH(CH_3)—^{2}C(=O)—^{1}CH_3$ — *3-Methyl-2, 4-pentanedione*

$^{6}CH_3—^{5}CH(CH_3)—^{4}CH_2—^{3}CH_2—^{2}CH(^{1}COOH)—Br$ — *2-Bromo-5-methylhexanoic acid*

$^{1}CH_3—^{2}CH_2—^{3}C(CH_3)(OH)—^{4}CH_2—^{5}CH_3$ — *3-Methyl-3-pentanol*

$H—C(=O)—C(=O)—H$ — *Ethanedial*

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$HO—\overset{O}{\overset{\|}{C}}—\overset{O}{\overset{\|}{C}}—OH$ — *Ethanedioic acid*

$^1CH_2 = {}^2CH—{}^3CH_2—{}^4C \equiv {}^5CH$ — *Pent-1-en-4-yne*

$^5CH_3—{}^4CH = {}^3CH—{}^2C \equiv {}^1CH$ — *Pent-3-en-1-yne*

$^5CH_3—{}^4CH(OH)—{}^3CH_2—{}^2C(=O)—{}^1CH_3$ — *4-Hydroxy-2-pentanone*

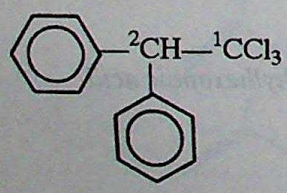
$^4CH_3—{}^3CH(CH_3)—{}^2CH(NH_2)—{}^1COOH$ — *2-Amino-3-methylbutanoic acid*

$^5CH_3—{}^4C(=O)—{}^3CH_2—{}^2CH_2—{}^1COOH$ — *4-Ketopentanoic acid*

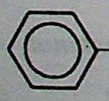
$^6CH_3—{}^5CH(CH_3)—{}^4C \equiv {}^3C—{}^2CH(OH)—{}^1CHO$ — *2-Hydroxy-5-methyl-3-hexynal*

$^8CH_3—{}^7CH(CH_3)—{}^6CH = {}^5CH—{}^4C(=O)—{}^3CH = {}^2CH—{}^1CH_3$ — *7-Methyl-octa-2, 5-dien-4-one*

$^5CH_3—{}^4CH(CHO)—{}^3CH_2—{}^2CH(CH_3)—{}^1COOH$ — *4-Formyl-2-methyl pentanoic acid*



— *1, 1, 1-Trichloro-2, 2-diphenylethane*

Here, the ring,  represents C_6H_5—, *i.e.*, phenyl group. For details see nomenclature of aromatic compounds. In case the phenyl group is further substituted, the carbon atoms of the ring are separately numbered starting from the carbon atom of the ring directly attached to the parent chain in such a way that substituent on ring gets lowest possible position. This has been illustrated in the following examples :

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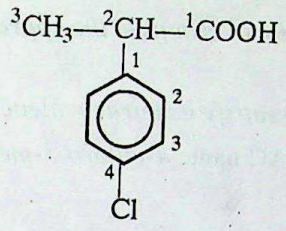
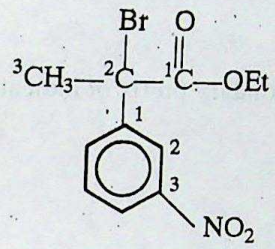
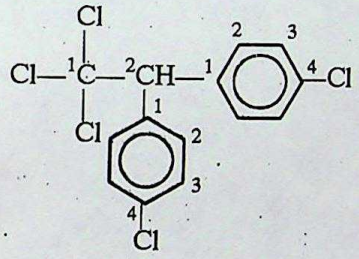


2-(4-Chlorophenyl) propanoic acid

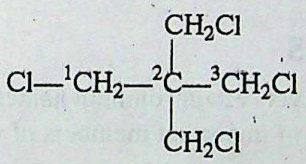


Ethyl 2-bromo-2-(3-nitrophenyl) propanoate

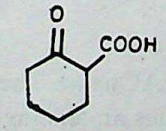
If the compound contains more than one similar complex radicals/substituents, then the numerical prefixes such as *di, tri* are replaced by *bis* and *tris* respectively. For example, in the following molecules two chlorophenyl radicals have been indicated by using the word *bis*.



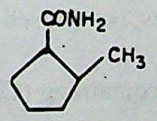
1, 1, 1-Trichloro-2, 2-bis (4-chlorophenyl) ethane



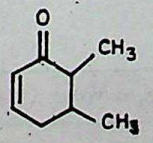
1, 3-Dichloro-2, 2-bis (chloromethyl) propane



2-Ketocyclohexanecarboxylic acid or *(2-Carboxycyclohexanone)*



2-Methylcyclopentanecarboxamide



5, 6-Dimethylcyclohex-2-en-1-one

WRITING THE STRUCTURE OF THE COMPOUND WHOSE NAME IS GIVEN

For writing the structure of the compound from the given IUPAC name the following steps are followed :

1. *Write the straight chain of carbon atoms with respect to the word root.*
2. *Number the carbon chain from either of the ends.*

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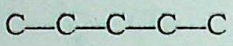
3. *Fill in the multiple bond* (if any) *and attach the substituents or functional groups at the appropriate positions.*

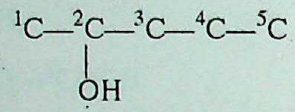
4. *Attach suitable number of hydrogen atoms to each carbon so as to satisfy its tetracovalency.*

For example, let us derive the structure of the compound having IUPAC name *4-chloro-3-methyl-2-pentanol* by following various steps.

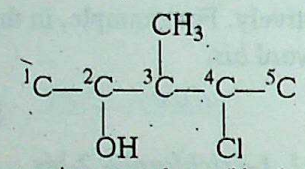
1. The word root '*pent*' indicates a chain of five carbon atoms.



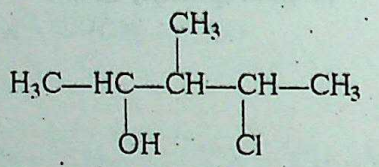
2. The primary suffix '*ane*' indicates, it is saturated compound and secondary prefix *ol* indicates, the presence of —OH group at carbon 2.



3. In addition, there is a —Cl group at carbon 4 and CH_3— at carbon 3.



4. Filling in the appropriate number of hydrogens, we get



COMMON OR TRIVIAL NAMES

Although IUPAC system of nomenclature has taken prime position yet certain common names are so familiar that they are so frequently used by chemists. The common names of important members of various families are given below :

1. ALKANES (PARAFFINS)

The first three members of this family have same common as well as IUPAC name. The higher members can exist as a number of isomers. The various isomers of butanes and pentanes are distinguished by use of prefixes *n*- (for normal), *iso*- and *neo*-. Prefix *n*- is used for straight chain alkanes, *iso*- is used for the molecules containing $(CH_3)_2CH$— (isopropyl) group and *neo*- is used for molecules containing $(CH_3)_3C$— group at the one end of the chain. Some examples are given below :

Molecular Formula	*Common Name*
$CH_3CH_2CH_2CH_3$	*n*-Butane
$(CH_3)_2CH—CH_3$	*iso*-Butane
$CH_3CH_2CH_2CH_2CH_3$	*n*-Pentane
$(CH_3)_2CHCH_2CH_3$	*iso*-Pentane

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Molecular Formula	*Common Name*
$CH_3-C(CH_3)_3$	*neo*-Pentane
$CH_3-CH(CH_3)CH_2CH_2CH_3$	*iso*-Hexane
$CH_3-C(CH_3)_2-CH_2CH_3$	*neo*-Hexane

The various isomers of hexane and higher alkanes cannot be differentiated by use of the prefixes *n*-, *iso* and *neo*-. This is due to the reason that with increase in number of carbon atoms, the number of isomers increases rapidly.

2. ALKENES (OLEFINS)

Molecular Formula	*Common Name*
$CH_2 = CH_2$	Ethylene
$CH_3-CH = CH_2$	Propylene
$CH_3-CH = CH-CH_3$	β-Butylene
$(CH_3)_2CH = CH_2$	*iso*-Butylene
$CH_2 = C = CH_2$	Allene

3. ALKYNES (ACETYLENES)

Molecular Formula	*Common Name*
$HC \equiv CH$	Acetylene
$CH_3C \equiv CH$	Methylacetylene (Allylene)
$CH_3CH_2C \equiv CH$	Ethylacetylene
$CH_3C \equiv CCH_3$	Dimethylacetylene (Crotonylene)

4. ALCOHOLS

Molecular Formula	*Common Name*
CH_3OH	Methyl alcohol
CH_3CH_2OH	Ethyl alcohol
$CH_3CH_2CH_2OH$	*n*-Propyl alcohol
$CH_3CH_2CH_2CH_2OH$	*n*-Butyl alcohol
$CH_3CH_2CH_2CH_2CH_2OH$	*n*-Amyl alcohol or *n*-Pentyl alcohol

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Molecular Formula	*Common Name*
$(CH_3)_2CH—CH_2—OH$	*iso*-Butyl alcohol
$CH_2 = CH—OH$	Vinyl alcohol
$CH_2 = CH—CH_2—OH$	Allyl alcohol
$CH \equiv C—CH_2—OH$	Propargyl alcohol

5. ALKYL HALIDES

Molecular Formula	*Common Name*
CH_3Cl	Methyl chloride
CH_3CH_2Cl	Ethyl chloride
$CH_2 = CH—Cl$	Vinyl chloride
$CH_2 = CH—CH_2—Br$	Allyl bromide

6. PRIMARY AMINES

Molecular Formula	*Common Name*
CH_3NH_2	Methylamine
$CH_3CH_2NH_2$	Ethylamine
$CH_3CH_2CH_2NH_2$	*n*-Propylamine

7. ISOCYANIDES

Molecular Formula	*Common Name*
CH_3NC	Methyl isocyanide
CH_3CH_2NC	Ethyl isocyanide

8. CARBOXYLIC ACIDS

Molecular Formula	*Common Name*
$HCOOH$	Formic acid
CH_3COOH	Acetic acid
CH_3CH_2COOH	Propionic acid
$CH_3CH_2CH_2COOH$	*n*-Butyric acid
$CH_3CH_2CH_2CH_2COOH$	*n*-Valeric acid
$(CH_3)_2CH—COOH$	*iso*-Butyric acid
$CH_2 = CH—COOH$	Acrylic acid

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9. ALDEHYDES

Molecular Formula	*Common Name*
$HCHO$	Formaldehyde
CH_3CHO	Acetaldehyde
CH_3CH_2CHO	Propionaldehyde
$CH_3CH_2CH_2CHO$	*n*-Butyraldehyde
$CH_3CH_2CH_2CH_2CHO$	*n*-Valeraldehyde
$(CH_3)_2CH—CHO$	*iso*-Butyraldehyde
$CH_2 = CH—CHO$	Acrolein
$CH_3CH = CH—CHO$	Crotonaldehyde

10. ACID CHLORIDES

Molecular Formula	*Common Name*
$HCOCl$	Formyl chloride
CH_3COCl	Acetyl chloride
CH_3CH_2COCl	Propionyl chloride

11. AMIDES

Molecular Formula	*Common Name*
$HCONH_2$	Formamide
CH_3CONH_2	Acetamide
$HCON(CH_3)_2$	N, N-Dimethyl formamide (DMF)
$CH_3CON(CH_3)_2$	N, N-Dimethyl acetamide
$CH_2 = CH—CONHCH_3$	N-Methyl acrylamide

12. ESTERS

Molecular Formula	*Common Name*
$H—C(=O)—OCH_3$	Methyl formate
$CH_3—C(=O)—OCH_3$	Methyl acetate
$CH_3—CH_2—C(=O)—OCH_3$	Methyl propionate
$CH_3CH_2CH_2CH_2—C(=O)—OC_2H_5$	Ethyl valerate

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13. ACID ANHYDRIDES

Molecular Formula	*Common Name*
$(CH_3CO)_2O$	Acetic anhydride
$(CH_3CH_2CO)_2O$	Propionic anhydride

14. CYANIDES

Molecular Formula	*Common Name*
CH_3CN	Acetonitrile
CH_3CH_2CN	Propiononitrile
$CH_3CH_2CH_2CN$	Butyronitrile

15. ETHERS

Molecular Formula	*Common Name*
$CH_3—O—CH_3$	Dimethyl ether
$CH_3—O—CH_2CH_3$	Ethyl methyl ether
$CH_3CH_2—O—CH_2CH_3$	Diethyl ether
$(CH_3)_2CH—O—CH(CH_3)_2$	Di-isopropyl ether
$CH_2 = CH—O—CH_2—CH = CH_2$	Allyl vinyl ether

16. KETONES

Molecular Formula	*Common Name*
CH_3COCH_3	Dimethyl ketone or Acetone
$CH_3COCH_2CH_3$	Ethylmethyl ketone
$CH_3CO—CH = CH_2$	Methyl vinyl ketone

17. SECONDARY AMINES

Molecular Formula	*Common Name*
$CH_3—NH—CH_3$	Dimethyl amine
$CH_3—CH_2—NH—CH(CH_3)_2$	Ethyl isopropyl amine

18. TERTIARY AMINES

Molecular Formula	*Common Name*
$(CH_3)_3N$	Trimethyl amine
$C_2H_5—N(CH_3)—C_2H_5$	Diethyl methyl amine

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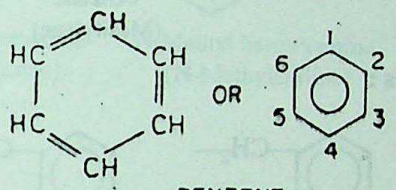
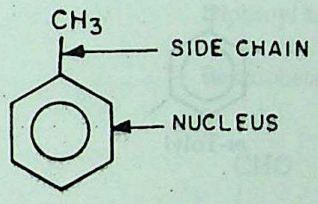
NOMENCLATURE OF AROMATIC COMPOUNDS

The term aromatic is derived from Greek work *aroma* which means pleasant smelling compounds. But in present form, the aromatic compounds are cyclic compounds which contain one or more benzene type rings. Benzene is the simplest hydrocarbon of aromatic series which has a planar cyclic ring of six carbon atoms having three double bonds in alternate positions as shown below :



BENZENE

The carbon atoms of benzene are numbered from 1 to 6 as shown above. The benzene ring is called the nucleus and alkyl groups attached to the ring are called side chains.



Benzene forms only one mono substituted derivative. However, it can form three disubstituted derivatives ; namely 1, 2 ; 1, 3 and 1, 4 derivatives. These are respectively called *ortho* (or *o*-), *meta* (or *m*-) and *para* (or *p*-) derivatives.

Tri and poly substituted derivatives are named by numbering the chain in such a way that the parent group gets the lowest number and sum of the positions of substituents is the smallest.

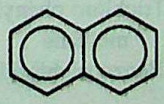
Nomenclature of Different Aromatic Families

The families of aromatic compounds are similar to those of aliphatic compounds. The names of some important members of each family are given below. Some of the common names are also given in brackets.

1. Hydrocarbons (*Arenes*)

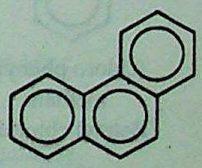
(*a*) *Hydrocarbons containing condensed rings*

Benzene



Naphthalene

Anthracene



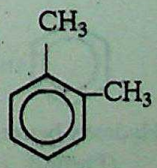
Phenanthrene

(*b*) *Hydrocarbons containing one ring only*

Methyl benzene (Toluene)

Ethyl benzene

Phenylethene (styrene)



1, 2-Dimethyl benzene (*o*-Xylene)

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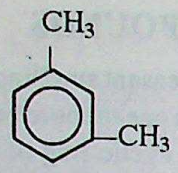
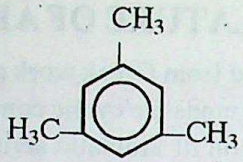
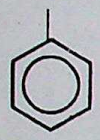


1, 3-Dimethyl benzene (*m*-Xylene)

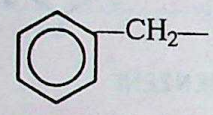


1, 3, 5-Trimethyl benzene (Mesitylene)

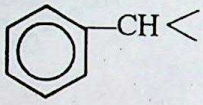
2. Aromatic or aryl radicals :



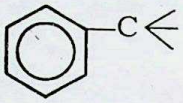
Phenyl radical



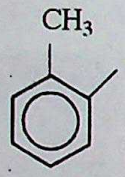
Benzyl (*monovalent*)



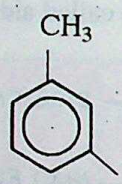
Benzal (*divalent*)



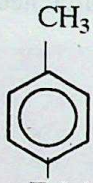
Benzo (*trivalent*)



o-Tolyl



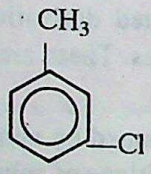
m-Tolyl



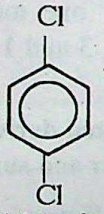
p-Tolyl

3. Halogen derivatives :

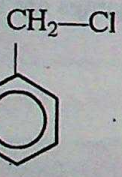
Chlorobenzene



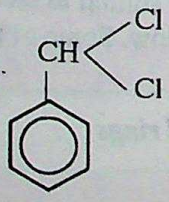
3-Chlorotoluene



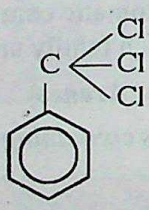
1, 4-Dichlorobenzene



Chloro phenyl methane (Benzyl chloride)



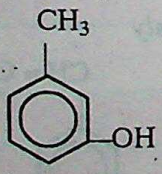
Dichloro phenyl methane (Benzal chloride)



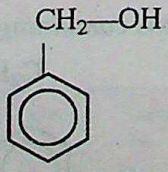
Trichloro phenyl methane (Benzo trichloride)

4. Phenols :

Hydroxy benzene (Phenol)



3-Hydroxy toluene (*m*-Cresol)



Phenylmethanol (Benzyl alcohol)

Here benzyl alcohol is not a phenol but an aromatic alcohol.

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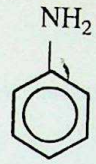
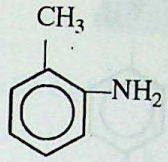
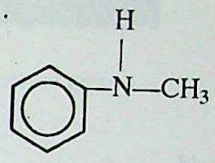
5. Amino derivatives :



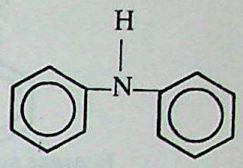
Benzenamine
(Aniline)



2-Methyl benzenamine
(2-Amino toluene)

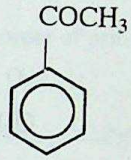


N-Methyl benzenamine
(N-Methylaniline)

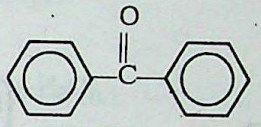


Diphenyl amine
(N-Phenylaniline)

6. Ketones :

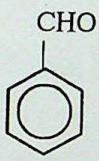


Methyl phenyl ketone
or
Acetophenone

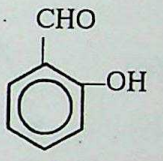


Diphenyl ketone
or
Benzophenone

7. Aldehydes :

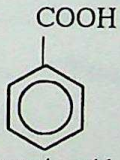


Benzaldehyde

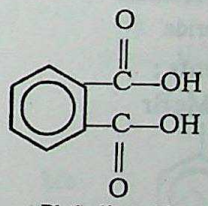


2-Hydroxy benzaldehyde
(Salicylaldehyde)

8. Carboxylic acids :

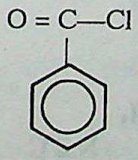


Benzoic acid

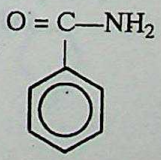


Phthalic acid
(1, 2-Benzene dicarboxylic acid)

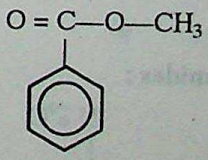
9. Acid derivatives :



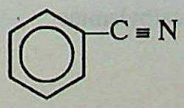
Benzoyl chloride



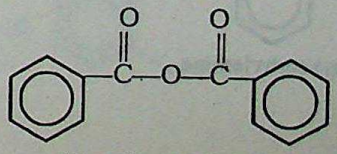
Benzamide



Methyl benzoate



Benzonitrile
(Phenyl cyanide)



Benzoic anhydride

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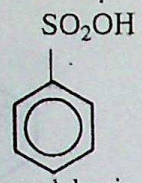
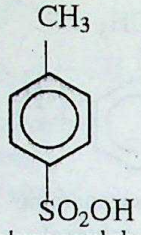
10. Sulphonic acids :

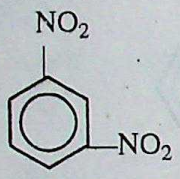


Benzene sulphonic acid

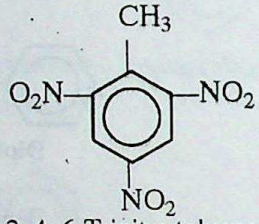


p-Toluene sulphonic acid (PTS)

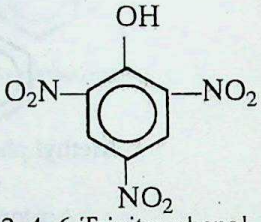
11. Nitro derivatives :



1, 3-Dinitro benzene

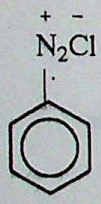


2, 4, 6-Trinitro toluene (T.N.T.)

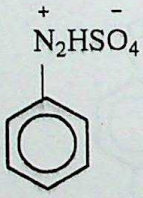


2, 4, 6-Trinitro phenol (Picric acid)

12. Diazonium salts :

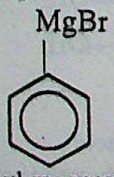


Benzene diazonium chloride

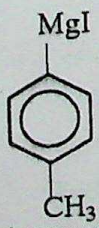


Benzene diazonium hydrogen sulphate

13. Grignard reagents :

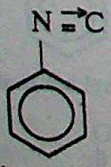


Phenyl magnesium bromide

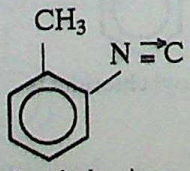


p-Tolyl magnesium iodide

14. Isocyanides :



Phenyl carbylamine



o-Tolyl carbylamine

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EXERCISES

1. Write the secondary suffixes for the following functional groups :

(*i*) —C ≡ N (*ii*) —C(=O)—Cl (*iii*) >C = O

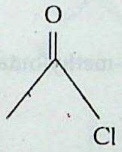
(*iv*) —C(=O)—H (*v*) —C(=O)—OH.

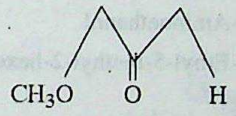
2. Write the correct order of priority of the following groups :

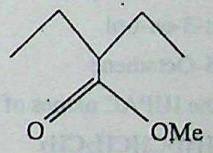
(*i*) —C ≡ N, —C(=O)—, —OH (*ii*) —CHO, —C(=O)—Cl, —SO_3H

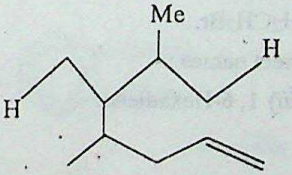
(*iii*) —C(=O)—OR, —C(=O)—NH_2, CHO.

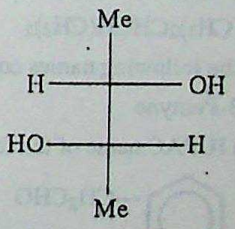
3. Write the correct IUPAC names of the following bond line formula :

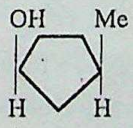
(*i*) 

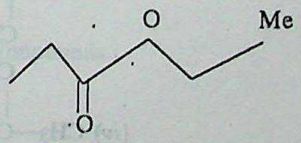
(*ii*) 

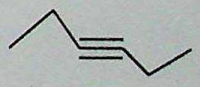
(*iii*) 

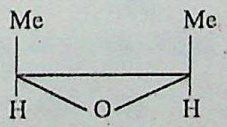
(*iv*) 

(*v*) 

(*vi*) 

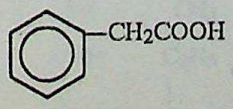
(*vii*) 

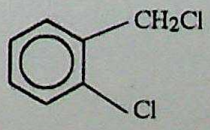
(*viii*) 

(*ix*) 

(*x*)

4. Give IUPAC names of the following :

(*i*) 

(*ii*) 

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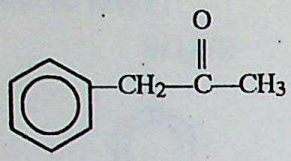
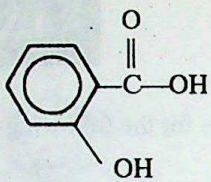
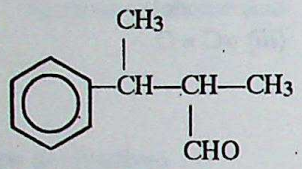
(iii) 

(iv) 

(v) 

5. Write the IUPAC names of the following compounds :

(i) $(CH_3)_2C = CH_2$ (ii) $(CH_3)_2CH—CH_2—CH_2Cl$ (iii) $(CH_3)_3COH$

(iv) $HOH_2C—CH = CH—CH_2OH$ (v) $(CH_3)_2CHCH_2CH(CH_3)_2$ (vi) $H_2C = C(CH_3)—CH_2—CH_2—OH$

(vii) $HC \equiv C—CH_2—CH_2—CH(Cl)—CHO$

6. Write the structural formulae of the following compounds :

(i) But-3-en-l-ol (ii) 2-Aminoethanol (iii) 2-Chloro-3-methylbutane

(iv) 3, 5-Octadiene (v) 4-Ethyl-5-methyl-2-hexene.

7. Write the IUPAC names of the following :

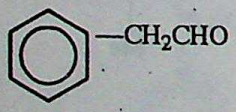
(i) $(CH_3)_2CHCH_2CH_3$ (ii) $(C_2H_5)_2CHCH_3$

(iii) $(CH_3)_2CHCH(CH_3)_2$ (iv) $(CH_3)_2C(Br)CH_2CH_2Br$.

8. Are the following names correct in IUPAC system ? If not write the correct names :

(i) 3-Pentyne (ii) 4, 4, 3-Trimethyl-1-hexyne (iii) 1, 6-Hexadiene.

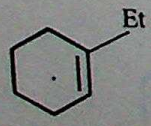
9. Give IUPAC name of the following :

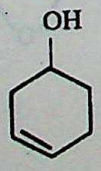
(i) 

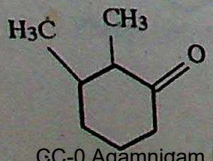
(ii) $CH_3—CH(CH_3)—CH(CH_3)—COOH$

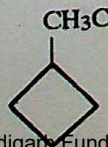
(iii) $CH_3—CH(CH_3)—CH_2Cl$

(iv) $CH_3—C(CH_3)(CHO)—CH_3$

(v) 

(vi) 

(vii) 

(viii) 

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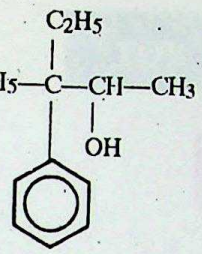
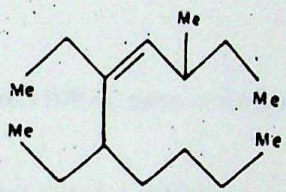
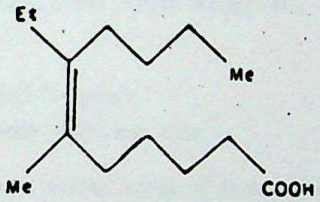
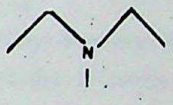
(*ix*) 

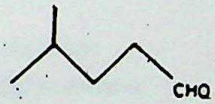
(*x*) $(CH_3)_2C(CCl_3)_2$

(*xi*) 

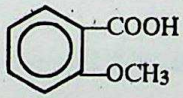
(*I.I.T. 1990*)

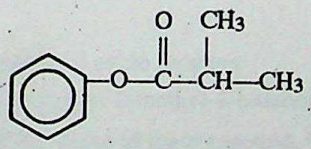
(*xii*) 

(*xiii*) 

(*xiv*) 

(*xv*) $CH_2(OH)—CH(OH)—CH_2(OH)$

(*xvi*) 

(*xvii*) 

10. Give IUPAC names of the following compounds :

(*i*) $CH_3—CH_2—CH(CH_3)—COOC_2H_5$ [*CBSE (O) 1994*]

(*ii*) $CH_3—CH(CH_3)—CH(CH_3)—CHO$ [*CBSE (O) 1994*]

(*iii*) $CH_3—CH(CH_3)—CO—CH(CH_3)—CH_3$ [*CBSE (O) 1994*]

(*iv*) $CH_3—C(C_2H_5)(Cl)—CH_2—C(C_2H_5)(Br)—CH_3$ (*CBSE 1995*)

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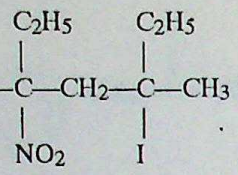
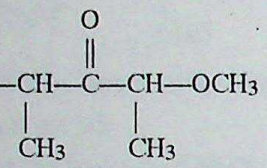
(*v*) 

(*CBSE 1995*)

(*vi*) $CH_3COCOOH$ (*P.S.E.B. 1995*)

(*vii*)

(*P.S.E.B. 1995*)

(*viii*) 

(*D.S.B.E. 1996*)

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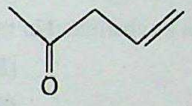
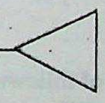
FOR THE COMPETITIVE EXAMINATION

MULTIPLE CHOICE QUESTIONS

1. The correct IUPAC name of the compound $CH_3CH(C_2H_5)CH(CH_3)CH_3$ is
   (*a*) 2-Ethyl-3-methyl butane (*b*) 2-isopropyl butane
   (*c*) 3, 4-Dimethyl pentane (*d*) 2, 3-Dimethyl pentane.
2. The IUPAC name for the compound, $CH_3CH = CH—CH(C \equiv CH)CH_3$ is
   (*a*) 4-Ethyl-2-pentene (*b*) 1-Ethyl-3-methyl-2- butane
   (*c*) 3-Methyl-4-hexen-1-yne (*d*) 4-Methyl-2-Hexen-5-yne.
3. The correct IUPAC name of the compound 
   (*a*) 4-penten-2-one (*b*) 3-Buten-1-al
   (*c*) 3-Acetyl propene-1 (*d*) Formyl propene.
4. The correct IUPAC name of the compound $CH_3CH_2C(OH)(CH_3)—CH_2$  is
   (*a*) ter-pentanol cyclo propane (*b*) 2-cyclobutyl-2-butanol
   (*c*) 1-cyclopropyl-2-methyl-2-butanol (*d*) 2- cyclobutyl-2-butanol.
5. The IUPAC name of the compound, $CH_2(OH)CH(NH_2)CO_2H$ is
   (*a*) 2-Amine-3-hydroxypropanoic acid (*b*) 1-Hydroxy-2-aminopropan-3-oic acid
   (*c*) 2-Amino-3-hydroxy propanoic acid (*d*) 1-Amino-2-hydroxy propanoic acid.
6. The correct IUPAC name of the Acrolein is
   (*a*) Ethanenitrile (*b*) Cyanomethane
   (*c*) Methanenitrile
   (*c*) Methanenitrile (*d*) Cyanoethane.
7. The IUPAC name of the compound, $CH_3CH_2N(H)(CH = O)$ is
   (*a*) Aldoethanamine (*b*) N-Formyl aminoethane
   (*c*) Ethyl formylamine (*d*) N-Ethyl methanamide.
8. The IUPAC name of $CH_3CH_2OCH_2C(=O)—H$ is
   (*a*) Formyl methyl ethyl ether (*b*) Ethyl aldomethyl ether
   (*c*) 2-Ethoxy formate (*d*) 2-Ethoxy ethanal.

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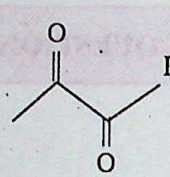
9. A student named certain compound as 2, 3-Dimethyl butane. It correct IUPAC name is
(*a*) 2, 3-dimethyl hexane (*b*) 3, 4-Diethyl hexane
(*c*) 2-Ethyl-3-methyl pentane (*d*) 2-Ethyl-butane.

10. The correct IUPAC name of  , is
(*a*) Ethanedial (*b*) 2-Ketopropanal
(*c*) 2, 3-Butanedione (*d*) Ethanedione.

11. The IUPAC name of Cl_3CCH_2CHO is
(*a*) Chloral (*b*) trichloropropanal
(*c*) 1, 1, 1-trichloropropanol (*d*) 3, 3, 3-trichloropropanal.

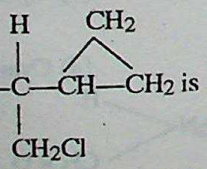
12. The IUPAC name of $CH_3—\underset{\underset{CH_2CH_3}{|}}{CH}—CH_2—CH(OH)—CH_3$ is
(*a*) 2-Ethylpentan-4-ol (*b*) 4-Ethylpentan-2-ol
(*c*) 4-methylhexan-2-ol (*d*) 4-methyl-2-hexanol.

13. When $—COOC_2H_5$ group is present as a substituent in the chain it shall be named
(*a*) ethoxy methanone (*b*) Ethyl methanoate
(*c*) Keto ethoxy (*d*) Ethyl carboxy.

14. Which group is always taken as a substituent in the nomenclature ?
(*a*) $—NH_2$ (*b*) $—NO_2$
(*c*) —CN (*d*) $—\overset{|}{C}=O$.

15. The principle functional group of following compound is
$$ClCH_2\overset{OH}{\overset{|}{C}}H\,CH_2—\overset{O}{\overset{\|}{C}}—CH_2NO_2$$
(*a*) Nitro (*b*) Alcohols
(*c*) Alkyl halides (*d*) Ketones.

16. 2-Methyl-1-butanol is the IUPAC name of
(*a*) sec-pentyl alcohol (*b*) ter-pentyl alcohol
(*c*) iso-pentyl alcohol (*d*) neo-amyl alcohol.

17. The correct IUPAC name of 
(*a*) 1-Chloro-2-butyl cyclo propane (*b*) 1-Chloro-2-cyclopropyl butane
(*c*) 1-Chloromethyl-1-ethyl cyclo propane (*d*) 3-Chloromethyl-1, 2-methylene pentane.

18. The correct IUPAC name of $CH_3—\overset{O}{\overset{\|}{C}}—O—\overset{O}{\overset{\|}{C}}—H$ is
(*a*) Acetyl methanoate (*b*) Formyl ethanoate
(*c*) ethoxy methanoate (*d*) Ethanoic methanoic anhydride

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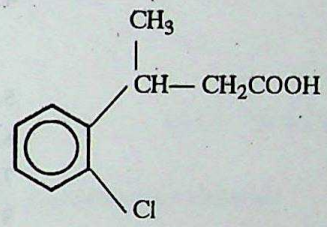
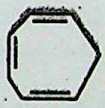
19. Iso octane is given correctly in structure
(*a*) $(CH_3)_3CCH(CH_3)CH_2CH_3$ (*b*) $(CH_3)_2CHCH(CH_3)CH(CH_3)_2$
(*c*) $(CH_3)_3CCH_2CH(CH_3)_2$ (*d*) $CH_3CH(CH_3)CH_2CH(CH_3)_2$.

FILL IN THE BLANKS

1. The IUPAC name of glyoxal is .....
2. The common name of $(CH_3)_2CHCH_2CH_2OH$ is .....
3. The compound $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-OH$ has functional group .....
4. The correct priority sequence followed among different acid derivative is .....
5. The name of substituent present in the compound  is .....
6. Grain alcohol is the common name of .....
7. The correct IUPAC name of $CH_2(COOH)-C(OH)(COOH)-CH_2$ is .....
8. The compound  has a correct IUPAC name .....
9. The correct structural formula of tetra methylene oxide is .....
10. The IUPAC name of cetane is .....

TRUE OR FALSE

1. The correct IUPAC name of allyl chloride is 3-chloro-1-propene.
2. The functional group —OH can be present on 1°, 2°, 3° or 4° carbon atom.
3. Homologues of a series has got the same formula.
4. The old name of methanol is Wood's spirit.
5. Dienes may have cumulated or conjugated double bonds in the molecule.
6. Propanal, $CH_3CH_2-C(=O)H$ is an unsaturated compound.
7. The IUPAC name of $CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-Cl$ is 1-chloro-1, 2-propadione.

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8. Esters are the compounds having a $-\overset{O}{\overset{\|}{C}}-$ and —OR groups in the compound at same or different positions.
9. Neohydrocarbons contain a quaternary carbon atom in chain.
10. An aromatic compound should obey $\{(4n + 2)\pi\}$ rule.

MATCH THE FOLLOWING

A. Benzene	1. C_6H_{12}
B. Pyridine	2. Nitriles
C. Glycol	3. Keto propanal
D. Cycloalkane	4. Alkanes
E. Alkyl cyanide	5. $CH_3-\overset{O}{\overset{\|}{C}}-C_6H_4-NH_2$
F. Methyl glyoxal	6. Heterocyclic
G. neo-amyl alcohol	7. Oxirane
H. Paraffins	8. Dihydric alcohol
I. Acetanilide	9. Aromatic
J. epoxide	10. primary alcohol.

ANSWERS

REVIEW PROBLEMS

7.1. (*i*) 3-chloro-1-propene (*ii*) 1, 2, 3-Butane triol
(*iii*) 2-Methoxy-2, 3-dimethyl butanal (*iv*) 3-Aldo-2-methyl propanoic acid
(*v*) 2-Ethyl-3-methyl-3-hydroxy propanal or 2-Hydroxy methyl-2-methyl butanal
(*vi*) Ethyl-(2-oxo) propanoate (*vii*) 1-Methoxy-2, 3-butanedione
(*viii*) Formylmethanoic acid (*ix*) N-Chloro-N-ethyl methanamide
(*x*) 2-Ethyl-butane dinitrile.

7.2. (*i*) 1-Ethoxy-3-methoxy propane (*ii*) 2-Amino-3-hydroxy propanal
(*iii*) N-Ethyl ethanamide (*iv*) 3-Penten-1-yne
(*v*) 2-Hydroxy propanoic acid.

VERY SHORT ANSWER TYPE QUESTIONS

1. (*i*) nitrile (*ii*) oyl chloride (*iii*) one (*iv*) al (*iv*) oic acid
2. $-C\equiv N > -\overset{O}{\overset{\|}{C}}- > -OH$ (*ii*) $-SO_3H > COCl > CHO$ (*iii*) $-COOR > CONH_2 > CHO$
3. (*i*) Ethanoyl chloride (*ii*) Methyl ethanoate (*iii*) Methyl (-2-ethyl) butanoate
(*iv*) 5-Ethyl-4, 6-dimethyl heptene-1 (*v*) 2, 3-Butanediol

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(*vi*) 3-Methyl-cyclo-1-pentanol (*vii*) Ethyl propanoate
(*viii*) 3-Hexyne (*ix*) 2, 3-epoxybutane (*x*) Tetramethylene oxide.

4. (*i*) 2-phenyl ethanoic acid (*ii*) 2-chloromethyl-1- chlorobenzene or 2′-chlorophenyl chloromethane
(*iii*) 1-Phenyl-2-propanone (*iv*) 2-Hydroxy benzoic acid (*v*) 2-Methyl-3-phenyl butanal.

5. (*i*) 2-Methylpropene (*ii*) 1-Chloro-3-methylbutane (*iii*) 2-Methyl-2-propanol
(*iv*) But-2-en-1, 4-diol (*v*) 2, 4-Dimethylpentane (*vi*) 3-Methyl-but-3-en-1-ol
(*vii*) 2-Chlorohex-5-yn-1-al

6. (*i*) $HOH_2C—CH_2—HC = CH_2$ (*ii*) $H_2N—CH_2—CH_2OH$

(*iii*) $H_3C—\underset{\underset{CH_3}{|}}{CH}—\underset{\underset{Cl}{|}}{CH}—CH_3$ (*iv*) $CH_3CH_2—HC = CH—HC = CH—CH_2—CH_3$

(*v*) $H_3C—HC = CH—\underset{\underset{C_2H_5}{|}}{CH}—\overset{\overset{CH_3}{|}}{CH}—CH_3$

7. (*i*) 2-Methylbutane (*ii*) 3-Methypentane (*iii*) 2, 3-Dimethylbutane
(*iv*) 1, 3-Dibromo-3-methylbutane

8. (*i*) No, it should be 2-Pentyne (*ii*) No, it should be 3, 4, 4-Trimethyl-1-hexyne
(*iii*) No, it should be 1, 5-Hexadiene

9. (*i*) Phenylethanal (*ii*) 2, 3-Dimethylbutanoic acid (*iii*) 1-Chloro-2-methylpropane
(*iv*) 2, 2-Dimethylpropanal (*v*) 1-Ethylcyclohexene (*vi*) Cyclohex-3-en-1-ol
(*vii*) 2, 3-Dimethylcyclohexanone (*viii*) 2-Cyclobutylpropanal
(*ix*) 3, 3-Diphenyl-2-pentanol (*x*) 1, 1, 1, 3, 3, 3-Hexachloro-2, 2-dimethyl propane
(*xi*) 5, 6-Diethyl-3-methyl-4-decene (*xii*) 7-Ethyl-6-methyl-6-undecenoic acid
(*xiii*) N-Ethyl-N-methylethanamine (*xiv*) 4-Methylpentanal
(*xv*) 1, 2, 3-Propanetriol (*xvi*) 2-Methoxybenzoic acid (*xvii*) Phenyl 2-methyl propanoate

10. (*i*) Ethyl 2-methylbutanoate (*ii*) 2, 3-Dimethylbutanal (*iii*) 2, 4-Dimethyl-3-pentanone
(*iv*) 3-Bromo-5-chloro-3, 5-dimethylheptane (*v*) 3-Iodo-3, 5-dimethyl-5-nitroheptane
(*vi*) 2-Ketopropanoic acid (*vii*) 2-Chloro-3-hydroxy propanal
(*viii*) 2-Methoxy-4-Methyl-3-pentanone.

MULTIPLE CHOICE QUESTIONS

1. (*d*)	**2.** (*c*)	**3.** (*a*)	**4.** (*c*)	**5.** (*c*)	**6.** (*a*)
7. (*d*)	**8.** (*d*)	**9.** (*b*)	**10.** (*b*)	**11.** (*d*)	**12.** (*d*)
13. (*c*)	**14.** (*b*)	**15.** (*d*)	**16.** (*c*)	**17.** (*b*)	**18.** (*d*)
19. (*c*).					

FILL IN THE BLANKS

1. Ethanedial **2.** iso amyl alcohol **3.** $—\overset{\overset{O}{\|}}{C}—$ and —COOH
4. anhydride > ester > acid chloride > acid amide **5.** 2′-chloro phenyl
6. Ethyl alcohol **7.** 3-carboxy-3-hydroxy pentanedioic acid

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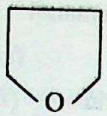
8. cycloheptatriene

9. $(CH_2)_4O$ or 

10. Hexadecane.

TRUE OR FALSE

1. True	2. False	3. False	4. True	5. True	6. False
7. False	8. False	9. True	10. True.		

MATCHING TYPE QUESTIONS

A—9 ; B—6 ; C—8 ; D—1 ; E—2 ; F—3 ; G—10 ; H—4 ; I—5 ; J—7.

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SOME GENERAL CONCEPTS

Organic reactions involve the transformation of one structure into another by rearrangement of atoms or change in bonds. Modern researchers have shown that organic reactions generally take place in more than one step. The description of various steps by which reactants change into the products is termed as **reaction mechanism.** The detailed study of the reaction mechanism is beyond the scope of the book, however, in this section we shall become familiar with some fundamental concepts associated with mechanism.

1. TYPES OF ATTACKING SPECIES

From mechanism point of view, the organic reactions proceed by the attack of certain active species on the reactant molecule (generally called *substrate*). These active species are called attacking species. They may be classified into three types :

(*i*) *Nucleophiles* (*ii*) *Electrophiles* (*iii*) *Free radicals.*

(*i*) **Nucleophiles (Nu).** These are neutral or negatively charged species which are capable of donating a pair of electrons to some other molecule. These species act as **Lewis bases** and attack the electron deficient centres of the organic molecule. Some examples are :

$$:\overline{C}l,\ :\overline{O}R,\ :\overline{C}N,\ :\overline{N}O_2,\ RCO\overline{O}:,\ :\overline{S}H,\ :\overline{O}H,\ :\overline{C}\equiv CR$$ **(Charged nucleophiles)**

$$H_2\ddot{O}:,\ R\ddot{O}H,\ \ddot{N}H_3,\ R\ddot{O}R,\ R\ddot{N}H_2,\ R_2\ddot{N}H,\ R_3\ddot{N}$$ **(Neutral nucleophiles)**

(*ii*) **Electrophiles (E).** These are neutral or positively charged species which are capable of accepting a pair of electrons from the substrate molecule. These species act as **Lewis acids** and attack the electron rich centres of the organic molecule. Some examples are :

$$\overset{+}{H},\ \overset{+}{Cl},\ \overset{+}{Br},\ Ar—\overset{+}{N}\equiv N,\ \overset{+}{N}O_2,\ \overset{+}{N}O$$ **(Charged electrophiles)**

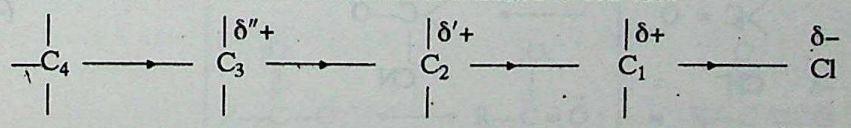
$$BF_3,\ AlCl_3,\ SO_3.$$ **(Neutral electrophiles)**

(*iii*) **Free radicals.** These are neutral species having an unpaired electron. Some examples are :

$$\dot{C}l,\ \dot{B}r,\ \dot{O}R,\ \dot{R},\ \dot{C}H_3.$$

2. INDUCTIVE EFFECT

Permanent displacement of electrons along a carbon chain when some atom or group of atoms with different electronegativity than carbon is attached to carbon chain is called inductive effect. For illustration consider a carbon chain which has a chlorine atom attached to one end.



(–I)-Effect

Since chlorine atom has higher electronegativity than carbon so the shared pair of electrons between C_1 and chlorine atom lies closer to chlorine atom as a result of which chlorine atom acquires a small negative charge and carbon atom C_1 acquires small +ve charge. As C_1 is now somewhat positively charged it attracts towards itself the shared pair of electrons between C_1 and C_2. This results in a small positive charge on C_2 also, but this charge is less than that on C_1. In this way electrons are displaced towards chlorine in the carbon chain. This type of displacement of electrons along a carbon chain is known as **Electron Withdrawing Inductive Effect** or **(–I) effect.**

If the electronegativity of the atom or group of atoms attached to the carbon chain is less than the electronegativity of the carbon then the displacement of electrons takes place away from group along the

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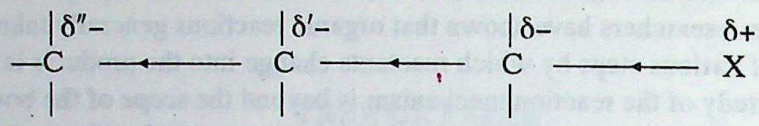
C-chain and this effect is called **Electron Releasing Inductive Effect** or **(+ I)-effect.** This inductive effect can be represented as shown below :



(+ I)-Effect

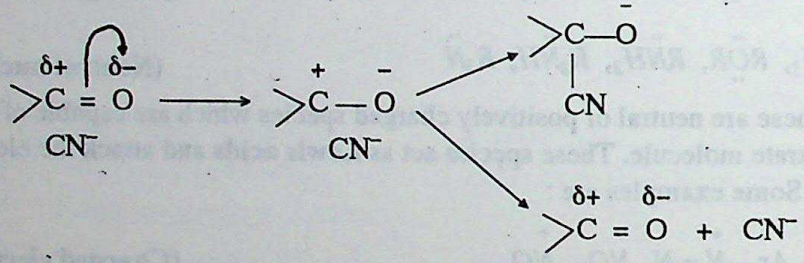
Inductive effect is a permanent effect and decreases rapidly as the distance from the source increases. Some of the groups which show inductive effect are given below :

– I effect : —NO_2 > —F > —Cl > —Br > —I > —OCH_3 > —C_6H_5

+ I effect : —$C(CH_3)_3$ > —$CH(CH_3)_2$ > C_2H_5 > —CH_3

3. ELECTROMERIC EFFECT

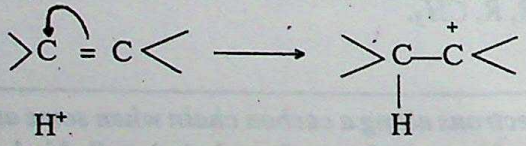
The complete transfer of the shared pair of π electrons of a multiple bond to one of the atoms in the presence of the attacking agent is called electromeric effect. For example, in the presence of some nucleophile the π electron pair of carbonyl group in aldehydes and ketones is transferred to oxygen. This effect is a temporary effect and takes place only in the presence of the attacking agent. If the attacking agent moves away without reacting with the molecule then the molecule returns to its original state.



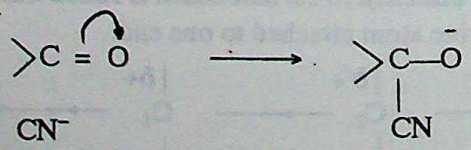
[Attacking agent reacts]

[Attacking agent moves away without reacting]

If the transferrence of electrons takes place towards the attacking agent it is called (+ E) effect and if it takes place away from the attacking agent then it is called (– E) effect. Electrons are always transferred towards the more electronegative atom of the two atoms between which the π bond exists.



(+ E)—Effect



(– E)—Effect

4. RESONANCE

Sometimes it is not possible to assign a single electronic structure to a molecule that may account for all its properties. In such a case the molecule is represented by two or more electronic structures but none of these represents the actual structure of the molecule. The actual structure of the molecule lies somewhere in between these structures but cannot be expressed on paper. Such a molecule is said to exhibit resonance. The various structures assigned to the molecule are called ***contributing structures*** or ***canonical structures*** whereas the intermediate structure is called ***Resonance hybrid***. For example, benzene (C_6H_6) molecule may be assigned following two structures :

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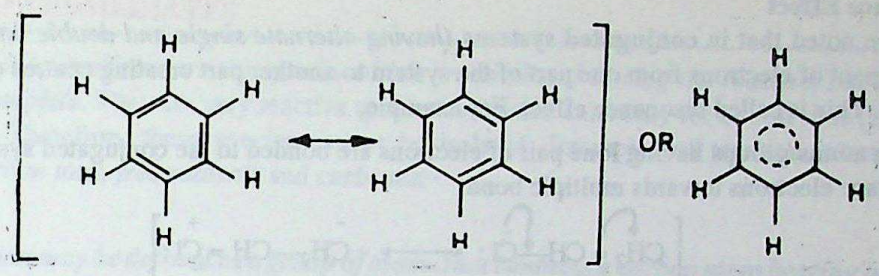
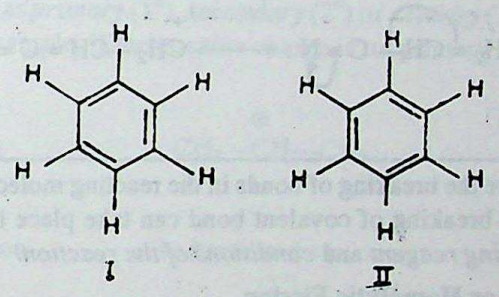


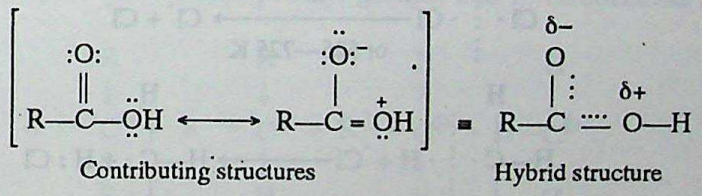
Any of these structures alone cannot account for all the properties of benzene. According to these structures there should be three single bonds (1.54 Å) and three double bonds (1.34 Å) between carbon atoms. But actually it has been found that all the six carbon-carbon bonds in benzene have same bond length (1.39 Å). The actual structure of benzene is resonance hybrid of the above two structures and may be represented as under :



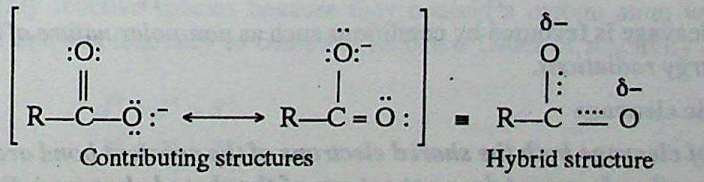
The resonance hybrid is more stable than any of the contributing structures and the difference between the energy of the most stable contributing structure and resonance hybrid is called ***resonance energy***.

Carboxylic acids and carboxylate ions also exhibit resonance.

Carboxylic acid



Carboxylate ion



Some important features of resonance are :

1. The various contributing structures may differ only in electronic arrangement but should have same arrangement of atoms.
2. The number of unpaired electrons should be same in all the contributing structures.
3. All contributing structures should have almost same energy.
4. The more stable contributing structure makes more contribution.
5. The bond distances of hybrid structure are intermediate of those of resonating forms.

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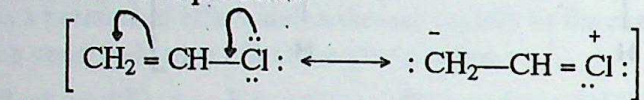
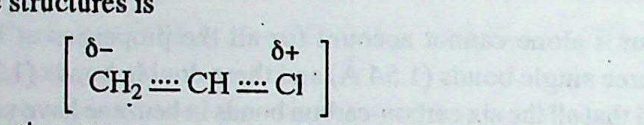
Resonance Effect

It may be noted that in **conjugated systems** (*having alternate single and double bonds*) resonance causes displacement of electrons from one part of the system to another part creating centres of high and low electron density. This is called resonance effect. For example,

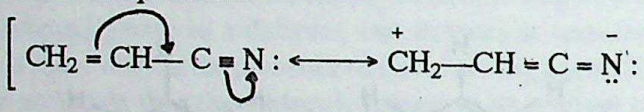
(*i*) When atoms/groups having lone pair of electrons are bonded to the conjugated system by a single bond, they displace electrons towards multiple bond.



The hybrid of above structures is



(*ii*) When electronegative atoms or group are bonded themselves to the conjugated system by multiple bond they pull electrons from the multiple bond.

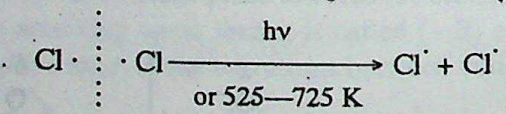


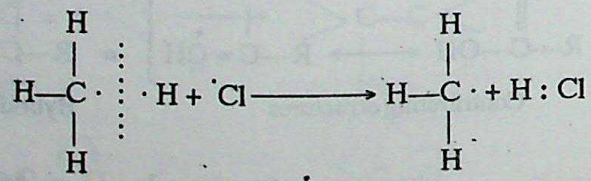
5. CLEAVAGE OF BONDS

Organic reactions involve the breaking of bonds in the reacting molecules and formation of new bonds to give product molecules. The breaking of covalent bond can take place in two ways depending upon the *nature of bond, nature of attacking reagent* and *conditions of the reaction.*

1. Homolytic Cleavage or Homolytic Fission

In this type of cleavage each fragment formed as the result of cleavage gets one electron from the shared pair of electrons. This type of cleavage results in the formation of species with odd or unpaired electrons. Such species are called free radicals. Some examples of homolytic cleavage are given below :

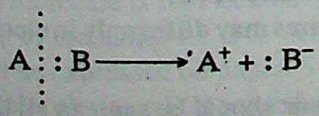




Homolytic cleavage is favoured by conditions such as *non-polar nature of bond, high temperature or presence of high energy radiations.*

2. Heterolytic cleavage

In this type of cleavage both the shared electrons of the covalent bond are taken away by one of the fragments (while the other fragment does not get any of the shared electrons). For example,



This type of cleavage results in the formation of charged species. Heterolytic cleavage in favoured by the conditions such as *polar nature of bond* and *presence of polar solvent.*

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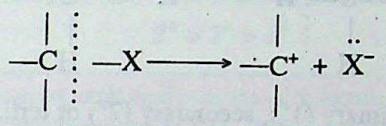
6. REACTION INTERMEDIATES

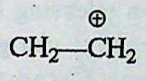
Reaction intermediates are the species which are produced during the reaction but are lost before the reaction is complete. They are very reactive species and hence exist only for a short time (10^{-6} seconds to a few seconds). Therefore, these species cannot be isolated. Examples of reaction intermediates are : *carbocations, carbon ions, free radicals* and *carbenes.*

Carbocations

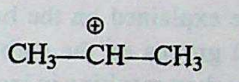
Carbocation may be defined as a group of atoms that contains a carbon atom bearing positive charge and containing only six electrons in its valence shell. These ions are formed by heterolytic cleavage in which the leaving group takes along with it the shared pair of electrons.



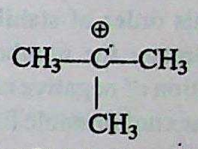
Carbocations are classified as ***primary*** (1°), ***secondary*** (2°) or ***tertiary*** (3°) depending upon the carbon bearing the positive charge. For example, if the positive charge is on primary carbon then the carbocation is primary.



Ethyl carbocation (1°)

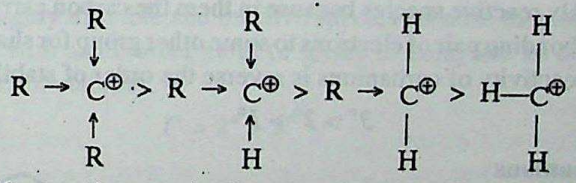


iso-Propyl carbocation (2°)



tert-Butyl carbocation (3°)

Decreasing order of stability of carbocations is 3° > 2° > 1°. This order of stability can be explained on the basis dispersal of positive charge by electron releasing inductive effect of alkyl groups. Greater the number of alkyl groups on the carbon carrying +ve charge greater would be dispersal of charge and hence more stable the carbocation would be .3° carbocations with three alkyl groups are most stable due to maximum dispersal of charge followed by 2° carbocations (2 alkyl groups) and 1° carbocations (1 alkyl group) as illustrated below :



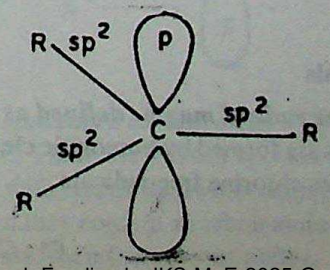
Carbocations are highly reactive species because they contain a carbon atom which has only six electrons in its valence shell and has tendency to complete its octet. Order of reactivity of carbocations is reverse the order of stability.

1° > 2° > 3° —*order of reactivity*

3° > 2° > 1° —*order of stability*

Orbital Structure of Carbocations

Electron deficient carbon in carbocations is bonded to three other atoms directly and for this bonding it uses sp^2 hybridised orbitals. This part of the carbocation is therefore planar. In addition to this there is a vacant *p*-orbital perpendicular to this plane with one lobe above the plane and the other below the plane as illustrated.



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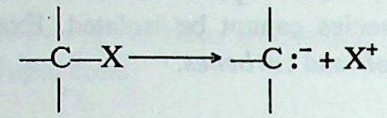
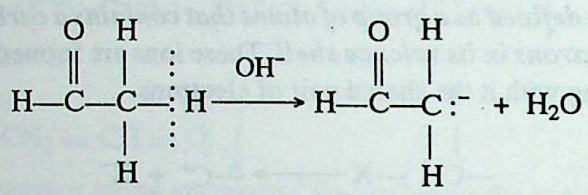
Carbanions

Carbanion may be defined as a group of atoms that contains a carbon atom bearing negative charge. Carbanions are formed by heterolytic cleavage in which shared pair remains with carbon atom.

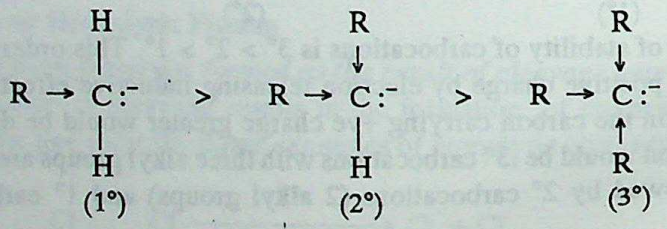




Carbanions are classified as primary (1°), secondary (2°) or tertiary (3°) after the carbon bearing the negative charge. For example, if the negative charge is on primary carbon then the carbanion is primary.

Decreasing order of stability of carbanions is 1° > 2° > 3°.

This order of stability can be explained on the basis of electron releasing inductive effect of alkyl groups. Greater the number of alkyl groups on the carbon bearing negative charge, greater would be the concentration of negative charge on carbon resulting in instability. Primary (1°) carbanion with only one alkyl group is maximum stable followed by secondary (2°) (with two alkyl groups) and tertiary (3°) (with three alkyl groups).

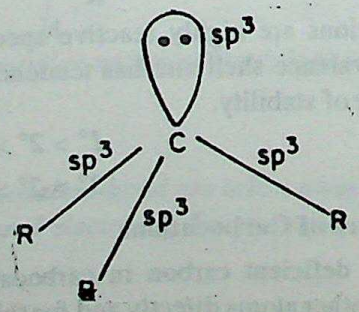


Carbanions are highly reactive species because in them the carbon carrying negative charge is electron rich and can donate its non-bonding pair of electrons to some other group for sharing. Hence, carbanions behave as nucleophiles. Order of reactivity of carbanions is reverse the order of stability.

$$3° > 2° > 1°$$ —*order of reactivity*

Orbital structure of carbanions

In carbanions the carbon carrying negative charge is sp^3 hybridised. Three sp^3 hybrid orbitals are used to form three σ bonds with three different atoms whereas the fourth sp^3 hybrid orbital accommodates lone pair.



Free Radicals

A free radical may be defined as an atom or group of atoms which contains an unpaired electron. Free radicals are formed by homolytic cleavage of a covalent bond. For example, in the presence of U.V. light, chlorine gives chlorine free radicals.

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$$Cl : Cl \xrightarrow{U.V.} 2Cl^{\bullet}$$

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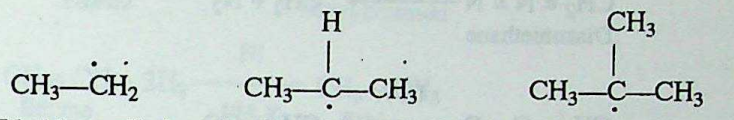
If the unpaired electron is on carbon atom then they are called alkyl free radicals. Alkyl free radicals are classified as primary (1°), secondary (2°) or tertiary (3°) after the the carbon atom carrying unpaired electron.

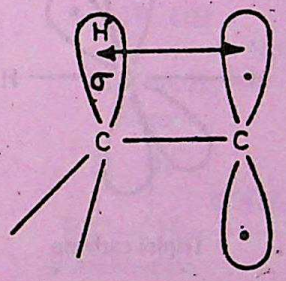


Ethyl free radical (1°) | *iso*-Propyl free radical (2°) | *tert*-Butyl free radical (3°)

Decreasing order of stability of alkyl free radicals relative to alkane from which they are formed is

$$3° > 2° > 1°$$ —*order of stability*

This order of stability can be explained in terms of delocalisation of unpaired electron through hyperconjugation. In hyperconjugation delocalisation takes place for through overlap of *p*-orbital containing unpaired electron with σ orbitals of alkyl groups.



Hyper conjugation

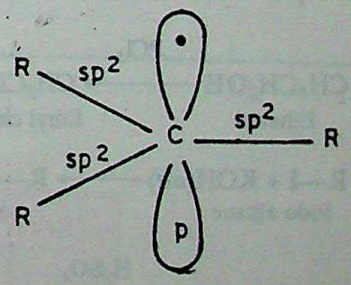
In 3° alkyl group radical there are three alkyl groups on the carbon carrying unpaired electron. Therefore, delocalisation of the unpaired electron through hyperconjugation is maximum and hence the radical is most stable followed by 2° radical (with two alkyl groups) and 1° radical (with one alkyl group).

Free radicals are highly unstable and reactive species because they contain one unpaired electron and have tendency to share it with some other atom or group to complete its octet. Order of reactivity of alkyl radicals is reverse the order of stability.

$$1° > 2° > 3°$$ —*order of reactivity*

Orbital structure

Structure of alkyl free radicals is not known with certainty but it is proposed that carbon carrying unpaired electron is sp^2 hybridised. These three sp^2 hybrid orbitals are used in forming three σ bonds with other atoms. The unpaired electron is present in the unhybridised *p*-orbital which is perpendicular to the plane of σ bonds.



Carbenes

A carbene may be defined as a group of atoms which contains a carbon atom with only six electrons in its valence shell, out of which two electrons are unshared. These are neutral species and are formed by removal of two monovalent groups or a divalent group along with one of the two bonding pairs of electrons. Carbenes are very unstable and highly reactive species because they contain a carbon atom which is deficient in electrons and has tendency to complete its octet. Carbenes are, therefore, electrophiles.

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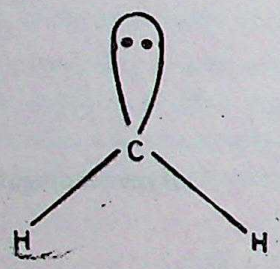
Due to their high reactivity, carbenes are generally produced in *situ*. Carbenes can be generated by photolysis of diazomethane or ketene.

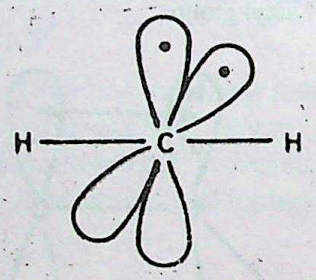
$$\underset{\text{Diazomethane}}{CH_2=\overset{+}{N}=\overset{-}{N}} \xrightarrow{U.V.} :CH_2 + N_2$$

$$\underset{\text{Ketene}}{CH_2=C=O} \xrightarrow{U.V.} :CH_2 + CO$$

Carbenes exist in two different states, singlet and triplet. In singlet state unshared electrons are paired whereas in triplet state they are not paired. ***Carbene in triplet state is more stable than carbene in singlet state.*** In singlet carbene, carbon atom carrying six valence electrons is sp^2 hybridised whereas in triplet it is *sp* hybridised.



Singlet carbene



Triplet carbene

7. TYPES OF ORGANIC REACTIONS

Organic reactions in general can be classified into four types :

(*a*) *Substitution reactions* (*b*) *Addition reaction*

(*c*) *Elimination reactions* (*d*) *Rearrangement reactions.*

(*a*) **Substitution reactions.** These reactions involve the replacement of an atom or group from the organic molecule by some other atom or group without changing the rest part of molecule. The product formed as a result of replacement is called **substitution product.** Some examples are :

(*i*) $\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{PCl_5} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} + POCl_3 + HCl$

(*ii*) $\underset{\text{Iodo alkane}}{R—I} + KOH(aq) \longrightarrow \underset{\text{Alcohol}}{R—OH} + KI$

(*iii*) $\underset{\text{Benzene}}{C_6H_5H} + HNO_3 \xrightarrow{H_2SO_4} \underset{\text{Nitrobenzene}}{C_6H_5NO_2} + H_2O$

(*b*) **Addition reactions.** These reactions are generally given by the organic molecules containing multiple bond. They involve the combination of two molecules to form a single molecule. In general, in these

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reactions one π-bond is cleaved and two sigma bonds are formed. The product formed is known as **addition product** or **adduct**. Some examples are :

(*i*)
$$\underset{\text{Ethene}}{CH_2 = CH_2} + HBr \longrightarrow \underset{\text{Ethyl bromide}}{CH_3CH_2Br}$$

(*ii*)
$$\underset{\text{Ethyne}}{CH \equiv CH} + 2H_2 \xrightarrow[575\ K]{Ni} \underset{\text{Ethane}}{CH_3—CH_3}$$

(*iii*)
$$\underset{\text{Acetaldehyde}}{CH_3\underset{\underset{H}{|}}{C} = O} + HCN \longrightarrow \underset{\text{Cynohydrin}}{CH_3\underset{\underset{OH}{|}}{CHCN}}$$

(*c*) **Elimination reactions.** These reactions involve the removal of two or more atoms/groups from the organic molecule under suitable conditions to form a product with multiple bond. Elimination can be considered as reverse of addition. Some examples are :

(*i*)
$$\underset{\text{Ethanol}}{H_2\overset{\overset{H}{|}}{C}—\overset{\overset{OH}{|}}{C}H_2} \xrightarrow{H_2SO_4} \underset{\text{Ethene}}{H_2C = CH_2} + \mathbf{H_2O}$$

(*ii*)
$$\underset{\text{Ethyl bromide}}{H_2\overset{\overset{H}{|}}{C}—\overset{\overset{Br}{|}}{C}H_2} \xrightarrow{KOH\ (alc.)} \underset{\text{Ethene}}{H_2C = CH_2} + \mathbf{HBr}$$

(*d*) **Rearrangement reactions.** These reactions involve the rearrangement of atoms within the molecule under suitable conditions to form the product with different properties. Some examples are :

(*i*)
$$\underset{\text{Ammonium cyanate}}{NH_4CNO} \xrightarrow{Heat} \underset{\text{Urea}}{(H_2N)_2C = O}$$

(*ii*)
$$\underset{n\text{-Butane}}{CH_3CH_2CH_2CH_3} \xrightarrow[Heat]{AlCl_3} \underset{\text{Isobutane}}{CH_3—\overset{\overset{CH_3}{|}}{C}H—CH_3}$$

EXERCISE

VERY SHORT ANSWER QUESTIONS
(1 Marks)

1. Explain what is homolytic fission.
2. What types of reagents are produced by heterolytic cleavage of bonds ?
3. What is inductive effect.
4. Why inductive effect is called transmission effect ?

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5. Give one example each of group/atoms having + I effect and – I effect.
6. What are electrophiles ? Give one example.
7. What are nucleophiles ? Give one example.
8. Name the different type of carbonium ions formed by formula $C_4H_9^+$ ion.
9. What are free radicals ?
10. What is electromeric effect ?
11. Give two differences between inductive effect and electromeric effect.
12. What is + E effect ? Give one example.
13. Name the different types of reactions taking place in organic compounds.
14. Name the two types of substitution reactions taking place in organic compounds.
15. What is SN^1 type of reaction ?
16. What is elimination reaction ? Give one example.
17. What are carbanions ?
18. Arrange different types of carbanions in increasing order of stability.
19. Name the kind of effect that operates to explain the stability of carbonium ions.
20. What are carbenes ?
21. What is singlet carbene and triplet carbene ?
22. What is hyper conjugation ?
23. What is difference between a free radical and an ion ?
24. What are addition reactions ?
25. What type of addition reactions occur in carbonyl compounds ?

DESCRIPTIVE QUESTIONS
(2, 3 Marks)

26. Explain the stability order of carbocations, giving reasons.
27. Classify the following into electrophillic and nucleophillic reagents

    (*a*) Cl^+ (*b*) $\overset{+}{N}O_2$ (*c*) $\overset{-}{\ddot{C}}N$ (*d*) $R\ddot{\underset{..}{O}}H$.
28. Explain briefly what is SN^2 type of reaction ?
29. Discuss the mechanism of addition of chlorine in CCl_4 to ethene.
30. Arrange the different carbonions ions in the decreasing order of stability giving reasons ?
31. Explain,

    (*i*) secondary amine is more basic than primary amine

    (*ii*) β-chloro propionic acid is weaker than α-chloro propionic acid.
32. What is + E and – E effect ? Explain with one example in each case.
33. Explain,

    (*i*) Ethene is more reactive than propene (*ii*) Formic acid is more acidic than acetic acid.
34. What are free radicals ? Discuss the stability order of primary, secondary and tertiary free radicals ?
35. What are rearrangement reactions ? Discuss with one example.

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FOR THE COMPETITIVE EXAMINATION

MULTIPLE CHOICE QUESTIONS

1. Which of the following is not an electrophile ?
   (*a*) $\overset{\oplus}{Cl}$ (*b*) Na^+ (*c*) H^+ (*d*) BF_3.
2. A free radical is
   (*a*) neutral in character (*b*) shortly lived (*c*) paramagnetic (*d*) all the above.
3. Homolytic cleavage of a bond generates
   (*a*) free radicals (*b*) carbenes (*c*) carbonium ions (*d*) carbanions.
4. A nucleophile is
   (*a*) a Lewis acid (*b*) electron deficient specie
   (*c*) a positively charged specie (*d*) an electron rich specie.
5. Heterolytic clevage of a carbon-carbon bond produces
   (*a*) two carbonium ions (*b*) two free radicals
   (*c*) one cation and one anion (*d*) a free radical and carbanion.
6. In ethyl alcohol, the bond that under goes heterolytic cleavage most readily is
   (*a*) C—C (*b*) C—O (*c*) C—H (*d*) O—H.
7. Which out of the following pairs represents only electrophiles ?
   (*a*) H_3O^+ (*b*) H_2O, H^+ (*c*) NO_3^+, $-NH_2$ (*d*) OH^-, R—O—H.
8. What is the state of hybridisation of carbon in carbanion ?
   (*a*) *sp* (*b*) sp^2 (*c*) sp^3 (*d*) sp^2d.
9. Which amongst the following will be most stable ?
   (*a*) $CH_3\overset{+}{C}H_2$ (*b*) $(CH_3)_2\overset{+}{C}H$ (*c*) $(CH_3)_3C\overset{+}{C}H_2$ (*d*) $(CH_3)_3\overset{+}{C}$.
10. Which out of the following series contain only nucleophiles ?
    (*a*) H_2O, SO_3, H_3O^+ (*b*) NH_3, H_2O, ROH (*c*) NH_3, H_2O, $AlCl_3$ (*d*) CN^-, SO_3, OH^-.
11. The most stable carbonium ions from amongst the following is
    (*a*) $(CH_3)_2\overset{+}{C}H$ (*b*) $Ph_3\overset{+}{C}$ (*c*) $CH_3\overset{+}{C}H_2$ (*d*) $CH_2 = CH—\overset{+}{C}H_2$.
12. Which of the following species has electron releasing effect ?
    (*a*) —COOH (*b*) C_6H_5 (*c*) $—NO_2$ (*d*) $(CH_3)_2CH—$.
13. The displacement of electrons in a multiple bond in the presence of attacking reagent is called
    (*a*) Inductive effect (*b*) electromeric effect (*c*) Resonance (*d*) hyper conjugation.
14. Which of the following carbonium ions has the least stability ?
    (*a*) methyl (*b*) ethyl (*c*) ter-butyl (*d*) isopropyl.
15. Mark the odd reagent from amongst the following
    (*a*) $\overset{-}{C}N$ (*b*) $CH_3\ddot{O}H$ (*c*) $\ddot{N}H_3$ (*d*) SO_3.

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16. Which of the following is not an electrophile ?

(a) CH_2 (b) $\overset{+}{C}H_3$ (c) SO_3 (d) —SH.

17. Dehydration of alcohols involves

(a) free radical (b) carbonium ion (c) carbanion (d) carbene.

18. Alkenes readily undergo

(a) substitution reactions (b) addition reactions (c) elimination reaction (d) rearrangement reactions.

19. Which of the following exerts + I effect

(a) CH_3— (b) Cl— (c) —NH_2 (d) —NO_2.

20. The formation of cyanohydrin from ketone is an example of

(a) nucleophillic substitution (b) electrophillic substitution

(c) electrophillic addition (d) nucleophillic addition.

FILL IN THE BLANKS

1. Fission of covalent bond is of two types, ... or ..... .
2. Homolytic cleavage of bond produces ..... .
3. Heterolytic cleavage is more favourable when carbon is attached to an atom of ..... .
4. The ter. carbonium ion is ..... stable than sec. carbonium ion.
5. When a reaction is done in the presence of peroxides it proceeds through ..... .
6. Reaction of ethane with HCl to produce ethyl chloride is an example of ..... .
7. Electron rich species are called ..... and can ..... a ..... of electrons.
8. Dehydration of alcohols to alkenes is an example of ..... .
9. Carbon atom carrying a positive charge has ..... of electrons.
10. Inductive effect is ..... effect.

TRUE OR FALSE

1. Heterolytic cleavage of bond produces free radicals.
2. A carbanion has octet of electrons.
3. Ammonia is an electrophile.
4. Alkenes can give electrophillic as well as nucleophillic addition reactions.
5. Electromeric effect is a temporary effect.
6. The carbenes have six electrons and two positive charges.
7. In ter. carbonium ion the charge bearing carbon atom is sp^3 hybridised.
8. The inductive effect operates along the chain of carbon atoms in an organic compound having any number of carbon atoms.
9. All the nucleophiles are negatively charged.
10. The conversion of ethyl chloride to ethyl alcohol proceeds through SN^2 type of reaction.

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MATCH THE FOLLOWING

(A) $R-X+Y \longrightarrow R-Y+X$	1. Elimination
(B) $RCH_2CH_2X \longrightarrow RCH=CH_2+HX$	2. Condensation
(C) $R-\underset{\underset{R}{\vert}}{A}-B \longrightarrow R-A-B-R$	3. Substitution
(D) $RCH=O+H_2A \longrightarrow RCH=A+H_2O$	4. Addition
(E) $RCH=CHR'+AB \longrightarrow RCHA-CHB-R'$	5. Rearrangement
(F) $A-B \longrightarrow A^{+}+:B^{-}$	6. Free radical
(G) $CH_3\overset{\oplus}{C}H(CH_3)$	7. Heterolytic clevage
(H) $A\cdot\times A \longrightarrow A^{\circ}+A^{*}$	8. Carbene
(I) $CH_2N_2 \longrightarrow CH_2+N_2$	9. Nucleophile
(J) $CH_3\ddot{O}H$	10. Electrophile.

ANSWERS

MULTIPLE CHOICE QUESTIONS

1. (B)	2. (D)	3. (A)	4. (D)	5. (C)	6. (D)
7. (A)	8. (C)	9. (D)	10. (B)	11. (B)	12. (D)
13. (B)	14. (A)	15. (D)	16. (B)	17. (B)	18. (B)
19. (B)	20. (D)				

FILL IN THE BLANKS

1. homolytic, heterolytic	2. free radicals	3. different electronegativity
4. more	5. free radical mechanism	6. electrophillic addition
7. nucleophiles, donate, pair	8. elimination reaction	9. sextet
10. permanent		

TRUE OR FALSE

1. False	2. True	3. False	4. False	5. True	6. False
7. False	8. False	9. False	10. True		

MATCH THE FOLLOWING

A—3 ; B—1 ; C—5 ; D—2 ; E—4 ; F—7 ; G—10 ; H—6 ; I—8 ; J—9.

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7

Organic Chemistry Based on Functional Groups—I

(Haloalkanes, Haloarenes, Alcohols and Phenols)

LEARNING OBJECTIVES

In this Unit, we shall learn

- *the names of haloalkanes, haloarenes, alcohols and phenols according to IUPAC system of nomenclature ;*
- *the methods of preparation of the classes of compounds listed above ;*
- *the correlation of the variation in physical properties of these compounds with their structures ;*
- *the chemical properties of the classes of compounds stated above ;*
- *the chemistry of some important polyhalogen and polyhydroxy compounds.*

In the previous class, we learnt about hydrocarbons. These are considered as parent compounds. The other compounds can be considered as derivatives of hydrocarbons. In this unit, we shall study about halogen derivatives (*haloalkanes* and *haloarenes*) and hydroxy derivatives (*alcohols* and *phenols*) of hydrocarbons.

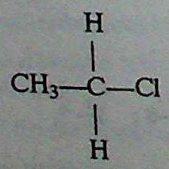
HALOALKANES AND HALOARENES

Alkyl halides or **haloalkanes** are the compounds in which a halogen is bonded to an aliphatic carbon. They have the general formula RX (where R is alkyl group, C_nH_{2n+1} and X is halogen atom). These may be obtained from an alkane by replacement of one hydrogen atom by a halogen atom.

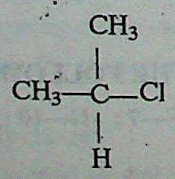
$$RH \xrightarrow[+X]{-H} RX$$

$$\underset{\text{Mathane}}{CH_4} \xrightarrow[+Cl]{-H} \underset{\text{Chloromethane}}{CH_3Cl}$$

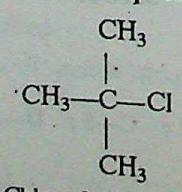
Alkyl halides are classified as primary, secondary and tertiary alkyl halides depending on whether the halogen atom is attached to a primary, secondary or tertiary carbon atom respectively. For example,



Chloroethane
(*Primary*)
(1°)



2-Chloropropane
(*Secondary*)
(2°)



2-Chloro-2-methyl propane
(*Tertiary*)
(3°)

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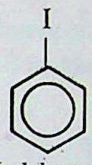
Aromatic halogen compounds are the halogen compounds which contain at least one aromatic ring. Halogen derivatives of aromatic compounds are of two types.

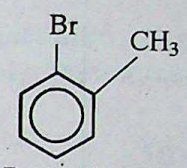
1. Aryl halides

In this type of compounds, the halogen atom is directly linked to the carbon of benzene nucleus. They are also called *nuclear substitution derivatives*. Some examples are :

Chlorobenzene



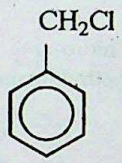
Iodobenzene



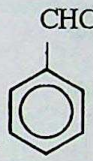
2-Bromotoluene

2. Aralkyl halides

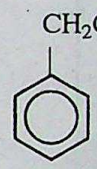
In this type of compounds, halogen is linked to the carbon atom of the *side chain*. They are also called side chain substitution derivatives. Some examples are :



Phenyl chloro-methane
Benzyl chloride



Phenyl dichloro-methane
Benzal chloride



1-Chloro-2-phenyl-ethane
β-Chloroethyl benzene

The side chain derivatives are very similar to aliphatic halogen derivatives *i.e.*, haloalkanes.

7.1. NOMENCLATURE

In the common system, aliphatic halogen derivatives are named as ***alkyl halides***. The words, *n-*, *sec-*, *ter-*, *iso-*, *neo-* and *amyl* are usually used in writing the common names*. In IUPAC system, they are considered as derivatives of corresponding alkanes and are named as ***haloalkanes***. The common and IUPAC names of some of the members of this class are given below :

Formula	*Common name*	*IUPAC name*
CH_3Cl	Methyl chloride	Chloromethane
CH_3CH_2Cl	Ethyl chloride	Chloroethane
$CH_3CH_2CH_2Cl$	*n*-Propyl chloride	1-Chloropropane
$(CH_3)_2CHCl$	*Iso*-Propyl chloride	2-Chloropropane
$CH_3CH_2CH_2CH_2Cl$	*n*-Butyl chloride	1-Chlorobutane
$CH_3-CH(Cl)-CH_2-CH_3$	*sec*-Butyl chloride	2-Chlorobutane

*The words *iso*-and *neo*- are used for the grouping of the kind $CH_3-CH(CH_3)-$ and $CH_3-C(CH_3)_2-CH_2-$ respectively.

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Formula	*Common name*	*IUPAC name*
$(CH_3)_2CH—CH_2—Cl$	*Iso*-Butyl chloride	1-Chloro-2-methylpropane
$(CH_3)_2C(CH_3)—Cl$	*tert*-Butyl chloride	2-Chloro-2-methylpropane
$CH_3CH_2CH_2CH_2CH_2Cl$	*n*-Pentyl chloride or *n*-Amyl chloride	1-Chloropentane
$CH_3CH(Cl)CH_2CH_2CH_3$	*sec*-Pentyl chloride or *sec*-Amyl chloride	2-Chloropentane
$(CH_3)_2CH—CH_2CH_2Cl$	*Iso*-Pentyl chloride or *Iso*-Amyl chloride	1-Chloro-3-methylbutane
$CH_3—C(CH_3)(Cl)—CH_2CH_3$	*tert*-Pentyl chloride or *tert*-Amyl chloride	2-Chloro-2-methylbutane
$CH_3—C(CH_3)_2—CH_2Cl$	*neo*-Pentyl chloride or *neo*-Amyl chloride	1-Chloro-2, 2-dimethylpropane

Apart from monohalides, the common names and IUPAC names of a few dihalides are also given below for ready reference.

Formula	*Common name*	*IUPAC name*
CH_2Cl_2	Methylene chloride	Dichloromethane
$CH_2Cl—CH_2Cl$	Ethylene chloride or Ethylene dichloride **(vic. dihalide)**	1, 2-Dichloroethane
$CH_3—CHCl_2$	Ethylidene chloride or Ethylidene dichloride	1, 1-Dichloroethane

It may be noted that *vic.* refers to *vicinal* and *gem.* refers to *geminal*. A **vicinal** dihalide has two halogen atoms on adjacent carbon atoms while **geminal dihalide** has two halogen atoms on the same carbon atom. In a chain of three or more carbon atoms if the halogen atoms are at terminal position it is not a *vic* dihalide. Such compounds are named as polymethylene dihalides. For example,

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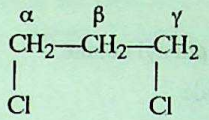
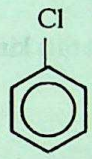


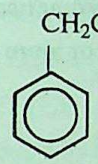
α, γ-Trimethylene dichloride

Haloarenes are named by prefixing the halogen and its position, if necessary, to the name of the parent aromatic compound.

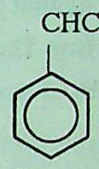
In writing the common names, the relative positions of the substituents at 1, 2- ; 1, 3- and 1, 4-positions are indicated by prefixes *ortho (o-), meta (m-)* and *para (p-),* respectively. The names of a few haloarenes are given below :



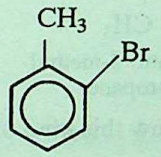
Chlorobenzene



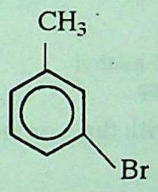
Phenyl chloromethane



Phenyl dichloromethane



2-Bromotoluene or *o*-Bromotoluene



3-Bromotoluene or *m*-Bromotoluene

4-Bromotoluene or *p*-Bromotoluene

REVIEW PROBLEMS

7.1. Give structural formula and IUPAC names of

(*a*) ter-amyl chloride (*b*) sec-butyl iodide

(*c*) neo-heptyl bromide (*d*) iso-pentyl chloride.

7.2. Write structural formula of

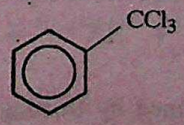
(*i*) 3-Bromohexane (*ii*) Neo pentyl iodide

(*iii*) Ethylene dibromide (*iv*) Iso propylidene chloride

(*v*) 2-chloro-3, 3-dimethyl butane.

7.3. Give common names of the following compounds :

(*i*) $(CH_3)_3C(CH_2)_2CH_2Br$ (*ii*) $(CH_2)_3Cl_2$

(*iii*) $CH_3\overset{Cl}{\overset{|}{C}}HCH_2Cl$ (*iv*) 

(*v*) $C_6H_5CH_2I$.

7.4. Name the different types of

(*a*) alkyl halides given by an organic compound $C_5H_{11}Br$.

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(*b*) Draw bond line structures of the following halides :

(*i*) sec-amyl chloride (*ii*) 2-chloro-2-phenyl butane

(*iii*) Allyl chloride (*iv*) Vinyl chloride

(*v*) Butylene chloride.

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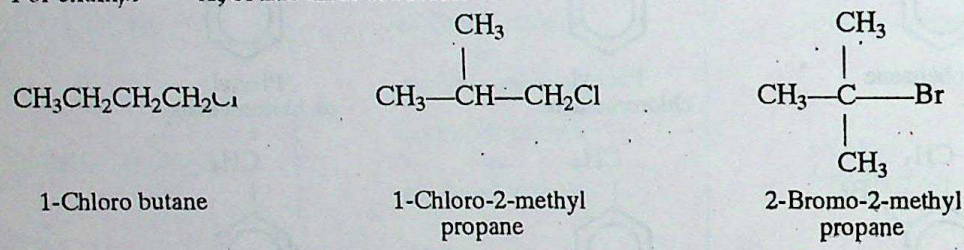
7.2. ISOMERISM IN HALOALKANES

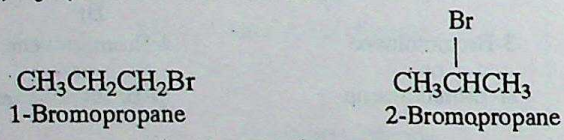
Haloalkanes can exhibit the following kinds of isomerism :

1. **Chain isomerism.** The haloalkanes with four or more carbon atoms exhibit this kind of isomerism. For example C_4H_9Cl has three isomers.



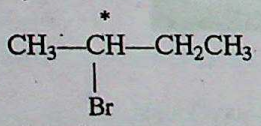
1-Chloro butane — 1-Chloro-2-methyl propane — 2-Bromo-2-methyl propane

2. **Position isomerism.** The haloalkanes with three or more carbons show this kind of isomerism. For example, C_3H_7Br has two isomerism.



1-Bromopropane — 2-Bromopropane

3. **Optical isomerism.** Haloalkanes having one asymmetric carbon give optical isomers. For example, sec-butyl bromide



(C = asymmetric carbon)

4. **Conformations.** Haloalkanes can also form conformers due to free rotation of C—C bond.

7.3. GENERAL METHODS OF PREPARATION OF HALOALKANES

Haloalkanes are prepared by the following methods :

1. From Alcohols

Different reagents can be used to get haloalkanes from alcohols as described below :

(*a*) **By reaction with halogen acids.** Alcohols can be converted into haloalkanes by treatment with halogen acids. The reaction, in general, can be represented as

$$\underset{\text{Alcohol}}{R—OH} + HX \longrightarrow \underset{\text{Alkyl halide}}{R—X} + H_2O$$

(*i*) **Chloroalkanes** are obtained by treating alcohols with HCl in the presence of anhydrous zinc chloride. *The anhydrous $ZnCl_2$ acts as dehydrating agent and thus favours the forward reaction* (Le Chateliar principle). The mixture of *HCl* and *anhydrous $ZnCl_2$* is known as *Lucas reagent.*

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$$CH_3CH_2OH + HCl \xrightarrow{\text{anhyd. } ZnCl_2} CH_3CH_2Cl + H_2O$$

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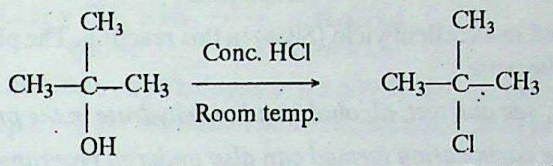
It must be noted that primary and secondary alcohols can be converted to their respective chlorides by using HCl and anhydrous $ZnCl_2$ (**Groove's process**). However, *tertiary* alcohols readily react with conc. HCl even in the absence of $ZnCl_2$.



tert-Butyl alcohol *tert*-Butyl chloride

(*ii*) **Bromoalkanes** can also be obtained in an identical manner by heating alcohols with KBr and conc. H_2SO_4. *HBr is generated in situ* (during the reaction) *by reaction of KBr or NaBr with conc.* H_2SO_4.

$$KBr + H_2SO_4 \longrightarrow KHSO_4 + HBr$$

$$C_2H_5\mathbf{OH} + HBr \longrightarrow C_2H_5Br + \mathbf{H_2O}$$

The reaction can also be carried out with conc. solution (48%) of hydrobromic acid.

(*iii*) **Iodoalkanes** are obtained by heating alcohols with KI and 95% H_3PO_4 (phosphoric acid).

$$\mathbf{KI} + H_3PO_4 \longrightarrow \underset{\text{Pot. dihydrogen phosphate}}{KH_2PO_4} + HI$$

$$C_2H_5OH + HI \longrightarrow C_2H_5I + H_2O$$

The reaction can also be carried out with conc. solution (57%) of hydroiodic acid.

Unlike alkyl chlorides, the secondary and tertiary bromides and iodides cannot be obtained from their respective alcohols. It is because the secondary and tertiary alcohols on heating with conc. H_2SO_4 undergo dehydration to form alkenes.

Reactivity of halogen acids towards this reaction is :

HI > HBr > HCl

It is because of the fact that the bond dissociation energy of HI is less than that of HBr which in turn is less than that of HCl.

Reactivity of alcohols towards this reactions is :

tertiary > secondary > primary

It is because of the fact that greater the number of electron releasing groups on α-carbon atom of alcohol, more is the polarity of C—OH bond. Consequently, greater is the ease with which it cleaves.

For **mechanism** of reaction of alcohol with halogen acid refer to sec. 7.16.

(*b*) **By reaction with phosphorus halides.** *Chloroalkanes* are obtained by reaction of alcohols with PCl_3 or PCl_5.

$$3CH_3CH_2OH + PCl_3 \longrightarrow 3CH_3CH_2Cl + H_3PO_3$$

$$CH_3CH_2OH + PCl_5 \longrightarrow CH_3CH_2Cl + POCl_3 + HCl$$

Bromo and *iodo alkanes* are obtained by reaction of alcohols with a mixture of red phosphorus and Br_2 or I_2. *The function of red phosphorus and* Br_2 *or* I_2 *is to get* PBr_3 *and* PI_3 *during the course of the reaction.* For example,

$$P_4 + 6Br_2 \longrightarrow 4PBr_3$$

$$\underset{\text{Ethanol}}{3CH_3CH_2OH} + PBr_3 \longrightarrow \underset{\text{Bromoethane}}{3CH_3CH_2Br} + \underset{\text{Phosphorus acid}}{H_3PO_3}$$

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$$P_4 + 6I_2 \longrightarrow 4PI_3$$

$$\underset{\text{1-Propanol}}{3CH_3CH_2CH_2OH} + PI_3 \longrightarrow \underset{\text{1-Iodopropane}}{3CH_3CH_2CH_2I} + H_3PO_3$$

The alkyl halides are obtained in excellent yield (80%) in this reaction. The phosphorus halide method is better than halogen acid method because

(*i*) *certain alcohols such as, sec and tert. alcohols tend to dehydrate in the presence of halogen acids.*

(*ii*) *in addition, intermediate carbocation formed can also undergo rearrangement in the presence of acids.*

(*c*) **By reaction with thionyl chloride.** In this method the alcohol is refluxed with thionyl chloride in the presence of a small amount of pyridine.

The reaction of straight chain primary alcohols in the presence or absence of pyridine is called **Darzen's procedure.**

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Chloroethane}}{CH_3CH_2Cl} + SO_2\uparrow + HCl\uparrow$$

Thionyl chloride is *preferred* in the preparation of alkyl chlorides because in this case the side products are gaseous and can be easily expelled during distillation. This results in the formation of chloroalkanes in pure state.

2. From Alkanes

When alkanes are treated with halogens, chlorine or bromine, in the presence of light or catalysts a mixture of mono- and poly-substituted products is obtained.

$$CH_4 \xrightarrow[-HCl]{Cl_2} CH_3Cl \xrightarrow[-HCl]{Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{Cl_2} CHCl_3 \xrightarrow[-HCl]{Cl_2} CCl_4$$

Although, the substitution beyond monohalogenation may be suppressed by controlling the ratio of halogen to alkane yet the method is not of much practical use because of the difficulties of separation of such a mixture.

In case of higher alkanes, different isomeric products are formed even when mono-substitution is carried out.

$$\underset{\text{Propane}}{CH_3CH_2CH_3} \xrightarrow{Cl_2} \underset{\substack{\text{1-Chloropropane}\\(45\%)}}{CH_3CH_2CH_2Cl} + \underset{\substack{\text{2-Chloropropane}\\(55\%)}}{CH_3\overset{\overset{Cl}{|}}{C}HCH_3}$$

In general, the ease of substitution in such cases is

tertiary H atom > sec. H atom > primary H atom

The *iodination* of alkanes is done by heating with iodine in the presence of oxidising agents like conc. HNO_3, HIO_4 or HIO_3. *The function of using such agents is to oxidize HI formed during the reaction to iodine, and hence shift the equilibrium in the forward direction.*

$$\underset{\text{Methane}}{CH_4} + I_2 \overset{\text{Heat}}{\rightleftharpoons} \underset{\text{Iodomethane}}{CH_3I} + HI$$

$$5HI + \underset{\text{Iodic acid}}{HIO_3} \longrightarrow 3I_2 + 3H_2O$$

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3. From Alkenes

Haloalkanes can be prepared from alkenes by the addition of halogen acids (HCl, HBr, HI).

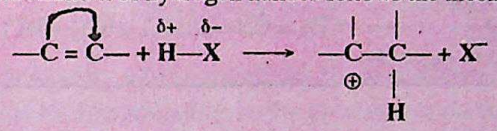
$$\underset{\text{Ethane}}{CH_2 = CH_2} + HI \longrightarrow \underset{\text{Iodoethane}}{CH_3CH_2I}$$

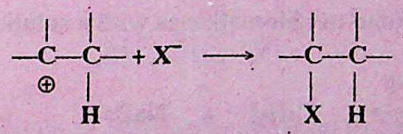
In unsymmetrical alkenes the addition of halogen acids takes place according to the **Markownikoff's rule.** The rule states that *negative part of the addendum molecule attaches itself to the carbon atom carrying less number of H atoms.*

$$\underset{\text{Propene}}{CH_3—CH = CH_2} + HBr \longrightarrow \underset{\text{2-Bromopropane}}{CH_3\overset{\overset{Br}{|}}{C}HCH_3}$$

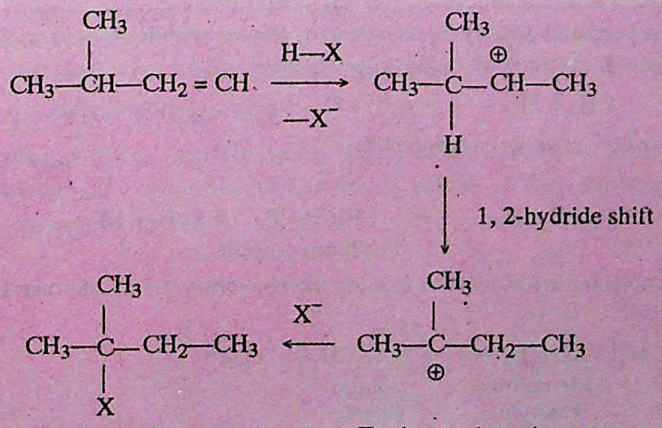
Mechanism

The electrophilic addition of hydrogen halides follows the mechanism as given below :

1. 

2. 

In certain cases the intermediate carbocation may undergo rearrangement through **1, 2-hydride shift** or **1, 2-methyl shift** to form more stable carbocation.



In the presence of organic peroxide such as *benzoyl peroxide* ($C_6H_5CO—O—O—COC_6H_5$) HBr reacts with alkyl halides to give the product against the Markownikoff's rule.

$$\underset{\text{Propene}}{CH_3—CH = CH_2} + HBr \xrightarrow{\text{Peroxide}} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br}$$

This is called **peroxide effect** or **Kharasch effect.**

It may be noted that the Kharasch effect applies to the addition of HBr only and not to the addition of HI or HCl.

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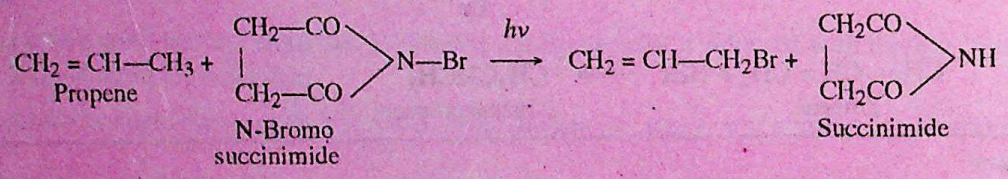
Allylic substitution

When alkenes are heated with Cl_2 or Br_2 at a high temperature of about 800 K, the hydrogen atom at allylic carbon is substituted with halogen resulting in the formation of allyl halides.

$$\underset{\text{Propene}}{CH_2=CH-CH_3} + Br_2 \xrightarrow{800\ K} \underset{\text{Allyl bromide}}{CH_2=CH-CH_2-Br} + HBr$$

The allylic substitution can also be carried out by treating the alkene with N-bromo succinimide (NBS) or sulphuryl chloride (SO_2Cl_2)



$$CH_2=CH-CH_3 + SO_2Cl_2 \xrightarrow[\text{traces of peroxide}]{475\ K,\ light} CH_2=CH-CH_2Cl + SO_2 + HCl$$

4. By Halide Exchange

Iodoalkanes can be obtained by treating bromo or chloroalkanes with a solution of sodium iodide in acetone or methanol. For example,

$$\underset{\text{Bromoethane}}{C_2H_5Br} + NaI \xrightarrow{\text{Acetone}} \underset{\text{Iodoethane}}{C_2H_5I} + NaBr$$

The reaction is known as **Finkelstein reaction.**

Fluoro alkanes are difficult to be prepared directly by the action of alkanes with F_2. *It is because fluorine has got a high reactivity towards the hydrogen.* It abstracts all the hydrogen atoms.

$$CH_4 + 2F_2 \longrightarrow 4HF + C$$

Also fluorination of hydrocarbons give unsatisfactory results.

$$CH_3CH_2CH_3 \xrightarrow{CoF_3} \underset{\text{Perfluoro propane}}{CF_3CF_2CF_3} + CoF_2 + HF$$

However, fluoro alkanes can be obtained in low yield by treating alkyl halides with salts like mercurous flouride, Hg_2F_2.

$$2CH_3CH_2Cl + \underset{\text{Mercurous fluoride}}{Hg_2F_2} \longrightarrow \underset{\text{Flouro ethane}}{2CH_3CH_2F} + Hg_2Cl_2$$

5. From Silver Salts of Fatty Acids

Bromoalkanes are obtained by this method by refluxing silver salts of fatty acids with bromine in CCl_4. For example,

$$\underset{\text{Silver propionate}}{CH_3CH_2COOAg} + Br_2 \xrightarrow[\text{Reflux}]{CCl_4} CH_3CH_2Br + CO_2 + AgBr$$

The reaction is known as **Borodine Hunsdiecker reaction** and can be employed for **descending of series.**

It may not be out of place to mention here that chloroalkanes can also be obtained by this reaction, however, the yield of chloroalkanes is usually low. Iodoalkanes, however, cannot be obtained by this reaction.

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It is because iodine forms esters with silver salt of fatty acids.

$2RCO_2Ag + I_2 \longrightarrow RCO_2R + CO_2 + 2AgI$. The reaction is known as **Birn baurn Simonini reaction.**

7.4. INDUSTRIAL PREPARATION

1. Chloroalkanes are prepared on industrial scale by direct chlorination of alkanes at high temperature. Though a mixture of various poly substituted products are obtained, these are not separated and are used as such as industrial solvents.

$$CH_4 + Cl_2 \xrightarrow{-HCl} CH_3Cl \xrightarrow[-HCl]{+Cl_2} CH_2Cl_2 \xrightarrow[-HCl]{+Cl_2} CHCl_3 \xrightarrow[-HCl]{+Cl_2} CCl_4$$

The chlorination of propane gives 1-chloropropane and 2-chloropropane.

$$CH_3CH_2CH_3 + Cl_2 \longrightarrow \underset{\text{1-Chloropropane}}{CH_3CH_2CH_2Cl} + \underset{\text{2-Chloropropane}}{CH_3\overset{\overset{Cl}{|}}{C}HCH_3}$$

2. Vinyl chloride, which is used for the manufacture of artificial rubber by polymerization, is obtained by the addition of HCl to acetylene in the presence of mercuric chloride.

$$CH \equiv CH + HCl \xrightarrow{HgCl_2} \underset{\text{Vinyl chloride}}{H_2C = CH—Cl}$$

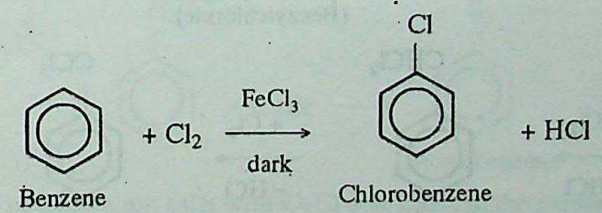
3. Allyl chloride is industrially prepared by chlorination of propene at high temperature (see method of preparation from alkenes, Section 7.3).

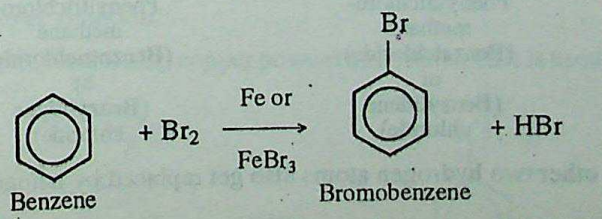
7.5. PREPARATION OF HALOARENES

Some important methods of preparation of haloarenes are being described as follows :

1. By Direct Halogenation

Haloarenes can be prepared by the direct halogenation of benzene in cold, dark and in the presence of halogen carrier or Lewis acids such as $FeCl_3$, $AlCl_3$, etc. In addition to these, iodine and iron fillings can also be used as halogen carriers.





*It must be noted that aryl fluorides cannot be obtained by this method because of the high affinity of fluorine for hydrogen. Also direct iodination is not possible except in the presence of oxidising agents like iodic acid, mercuric oxides, etc., for reasons as discussed earlier (Section 7.2).

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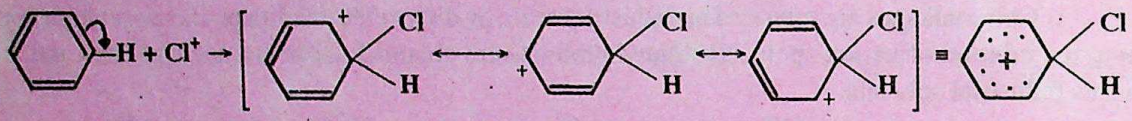
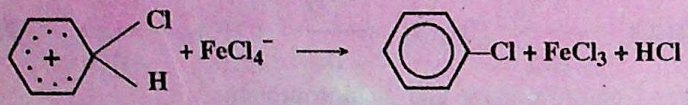
Mechanism of Halogenation

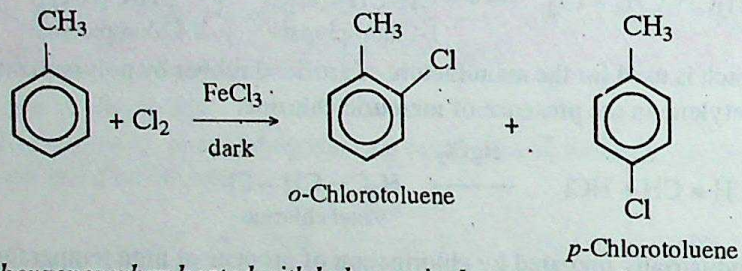
Halogenation of benzene is an electrophilic substitution reaction. The reaction takes place through the following steps :

1. $Cl_2 + FeCl_3 \longrightarrow FeCl_4^- + Cl^+$

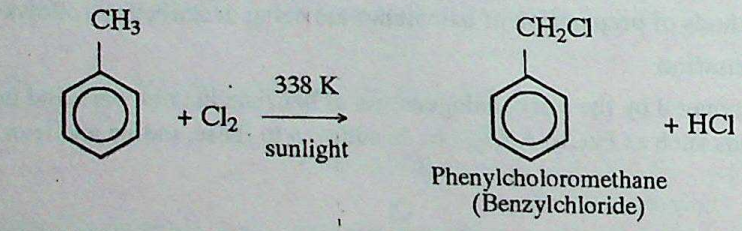
2. 

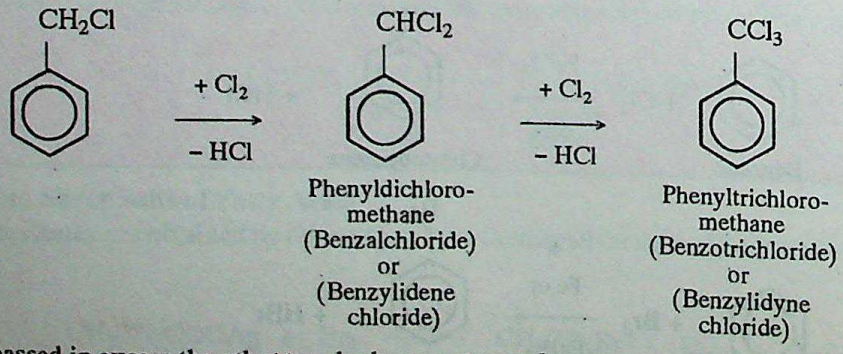
3. 

If toluene is used instead of benzene, the substitution takes place at *ortho*- or *para*-position because methyl group is ortho and para direction group.



The alkyl benzenes when heated with halogens in the presence of sunlight and in the absence of Lewis acids (halogen carrier) undergo substitution at the alkyl chain resulting in the formation of aralkyl halides. For examples, when Cl_2 is passed through boiling toluene in the presence of sunlight, substitution takes place in the side chain.





If Cl_2 is passed in excess the other two hydrogen atoms also get replaced by halogen atoms.

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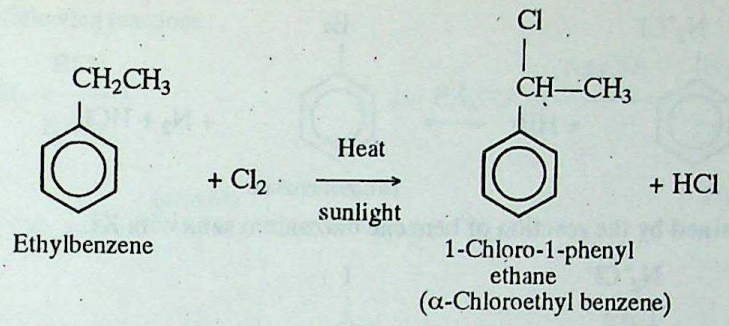
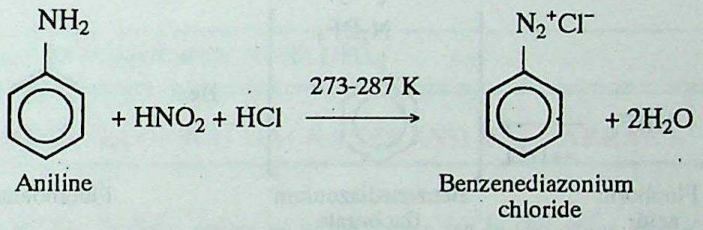


In case of ethyl benzene substitution takes place at benzylic position.

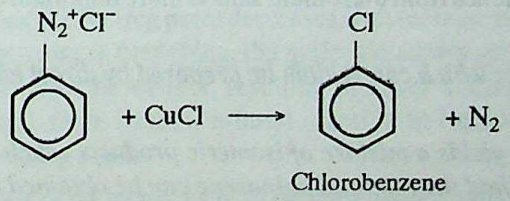
2. From diazonium compounds

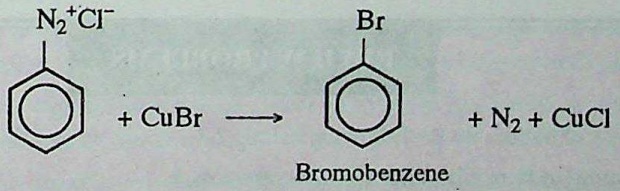
The method consists in first treating an amino compounds with nitrous acid ($NaNO_2$ + HCl) at low temperature (0° —4°C) when a diazonium salt is obtained.

$$NaNO_2 + HCl \longrightarrow HNO_2 + NaCl$$



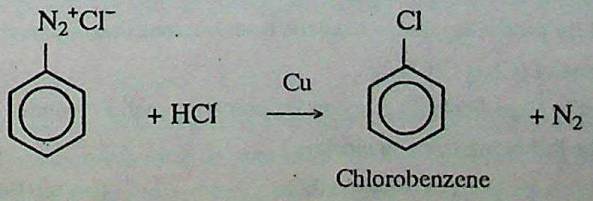
The resulting diazonium compound is treated with CuCl and HCl or CuBr and HBr to give the corresponding haloarene.





The reaction of diazonium salts with CuCl and CuBr in the presence of corresponding halogen acids is known as **Sandmeyer reaction.**

If instead of CuCl and CuBr, copper powder and HCl or HBr is used, the reaction is called **Gattermán's reaction.**



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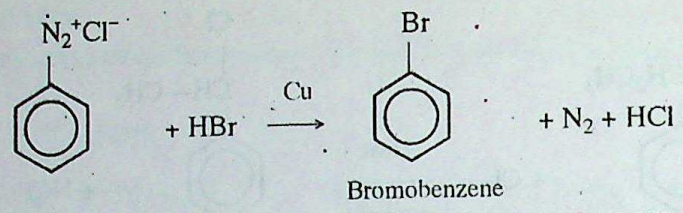
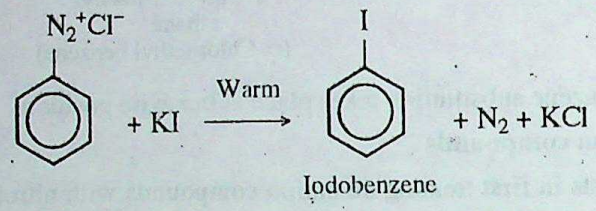
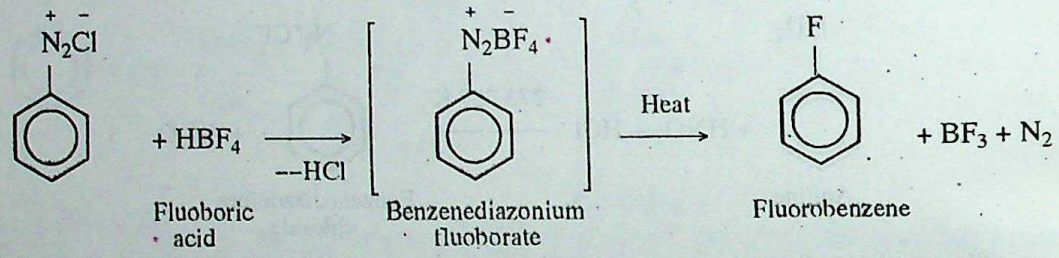


Iodoarenes are obtained by the reaction of benzene diazonium salts with KI.



Fluoroarenes are obtained by the reaction of corresponding diazonium salt with fluoboric acid to produce diazonium fluoborate which on heating produces fluorobenzene.



This reaction is called **Balz-Schiemann reaction.**

The preparation of haloarenes from diazonium salts is more important than direct halogenation because of the following two reasons :

(*i*) *Fluorides and iodides which can seldom be prepared by direct halogenation, can be prepared by this method.*

(*ii*) *Direct halogenation yields a mixture of isomeric products which are difficult to separate in pure forms but in this method the required haloarene can be obtained in a good yield.*

REVIEW PROBLEMS

7.5. To which category of halides do the following belong ?

(*i*) *p*-Tolylchloride (*ii*) Benzylbromide (*iii*) *Iso*-amyl iodide.

7.6. Which out of HCl and $SOCl_2$ is preferred for converting ROH to RCl.

7.7. The product formed by treatment of isobutylene with HI is .....

7.8. Which isomer of C_4H_9I is capable of showing enantiomerism ?

7.9. On chlorination of ethane, two isomeric dihalides are formed along with C_2H_5Cl. Give their structures.

7.10. Name the reagent used for producing fluoro-benzene from benzene diazonium chloride.

7.11. What is the IUPAC name of $(Cl_3)_2C(CH_3)_2$.

7.12. Name the reagents used in Hunsdiecker's reaction for preparing methyl bromide.

7.13. How will you obtain the following from an alcohol ?

(*i*) sec-Butyl chloride (*ii*) Fluoro ethane (*iii*) tert-Butyl iodide

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7.14. Complete the following reactions :

(*i*) $CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[ZnCl_2]{HCl} ?$

(*ii*) $CH_3COOH \xrightarrow{Ag_2CO_3} ? \xrightarrow[CCl_4]{Br_2} ?$

(*iii*) $CH_3CH = CH_2 + HCl \xrightarrow{\text{peroxide}} ?$

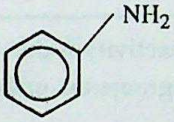
(*iv*)

$+ \; I^- \xrightarrow{(CH_3)_2C = O} ?$

(*v*)

$+ \; \overset{-}{O}H/\overset{-}{C_2H_5O} \longrightarrow ?$

(*vi*) $CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow[H_2SO_4]{KBr} ? \xrightarrow[475\ K]{SO_2Cl_2} ?$

(*vii*) 

$+ \; HNO_2 \longrightarrow ? \xrightarrow{HBF_4} ?$

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7.6. PHYSICAL PROPERTIES OF HALOALKANES AND HALOARENES

(*a*) **Haloalkanes**

(*i*) **Boiling points.** The boiling points of haloalkanes are in the order RCl < RBr < RI. *It is because with the increase in size and mass of the halogen atom the magnitude of van der Waal forces of attraction increases.*

Among isomeric alkyl halides, the boiling point decreases with increase in branching in the alkyl group. This is due to the reason that with increase in branching, the molecule attains spherical shape with less surface area. As a result interparticle forces become weaker, resulting in lower boiling point. For example, among isomeric butyl chlorides, the straight chain isomer, *n*-butyl chloride has the highest boiling point whereas *tert*-butyl chloride has the lowest boiling point.

For same halogen, the boiling point increases with increase in molecular mass.

Haloalkanes have higher boiling points as compared to those of corresponding alkanes. This is due to their polarity and strong dipole-dipole attractive interactions between haloalkane molecules.

(*ii*) **Solubility in water.** Although polar in nature, alkyl halides are insoluble in water *because they are not able to form hydrogen bonds with water molecules.*

However, they are soluble in organic solvents such as alcohols, ether and benzene.

(*iii*) **Density.** Alkyl chlorides are generally lighter than water whereas bromides and iodides are heavier. Their densities are in the order R—I > R—Br > R—Cl. Polychlorides are however, heavier than water.

(*b*) **Haloarenes**

(*i*) **Boiling points.** The boiling points of monohalogen derivatives of benzene, which are all liquids, follow the order

Iodo > Bromo > Chloro

The boiling points of isomeric dihalobenzenes are nearly the same. However, their melting points are quite different. ***The melting point of para isomer is generally 70—100 degrees higher than the melting points of ortho and meta isomers.*** *The higher melting point of para isomer is due to its symmetry which leads to more close packing of its molecules in the crystal lattice.*

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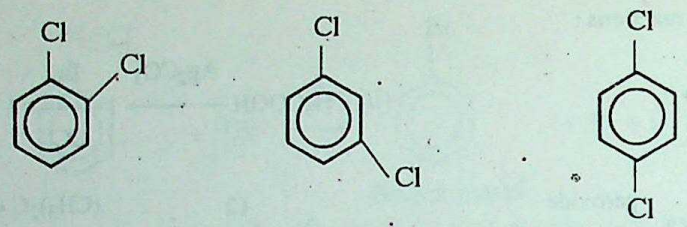


b.p.	453 K	446 K	448 K
m.p.	256 K	249 K	325 K

(*ii*) **Solubility.** Haloarenes are insoluble in water, acids or bases but are soluble in organic solvents.

(*iii*) **Density.** These are all heavier than water. Their densities follow the order, iodo > bromo > chloro.

7.7. CHEMICAL PROPERTIES

Haloalkanes are highly reactive class of aliphatic compounds. Their reactivity is due to the presence of *polar carbon-halogen bond* in their molecules. In general, for a given alkyl group, the **order of reactivity** decreases as :

iodides > bromides > chlorides

The explanation for the above order is based on the fact that most of the reactions of alkyl halides involve the cleavage of C—X bond. Now, larger the bond dissociation energy of C—X bond, smaller is the reactivity. The bond dissociation energy decreases with the increase in the size of halogen atom, i.e., **C—Cl > C—Br > C—I.** *Hence, the reactivity increases from alkyl chlorides to bromides and from bromides to iodides.*

C—X Bond	C—Cl	C—Br	C—I
Bond dissociation energy ($kJ\ mol^{-1}$)	328	275.6	240

The chemical reactions of haloalkanes can be divided into four types :

(*i*) *Nucleophilic substitution reactions*

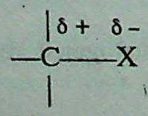
(*ii*) *Dehydrohalogenation*

(*iii*) *Reactions with metals*

(*iv*) *Reduction.*

I. Nucleophilic Substitution Reactions

In haloalkanes, the halogen atom is attached to the carbon atom. As the halogen atom is more electronegative than carbon, the bond between carbon and halogen is polar in character (supported by high dipole of the order of 2-2.2 D).



Due to the presence of partial positive charge on the carbon atom, the nucleophilies can attack on electron deficient carbon thereby resulting in the displacement of weaker nucleophile, the halide ion. Thus, typical reactions of alkyl halides are **nucleophilic substitution reactions.**

$$\underset{}{R:X} + \underset{\textbf{Nucleophile}}{:Z^-} \longrightarrow R:Z + \underset{\textbf{Halide ion}}{X^-}$$

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It must be noted that halide ions are substituted only if the attacking nucleophiles is stronger than it. Since halide ion itself is very very weak nucleophile the attacking nucleophile is generally stronger than it.

Mechanism

Nucleophilic substitution may take place in two ways.

(*i*) **SN^1 Mechanism** (*Unimolecular nucleophilic substitution*)

In this type, the rate of reaction is dependent only on the concentration of alkyl halide, *i.e.*,

$$\text{Rate} = k\,[RX]$$

The tertiary alkyl halides react by SN^1 mechanism via formation of carbocation as intermediate.

Step I. $$R{-}X \xrightarrow{\text{Slow}} R^+ + X^-$$

Step II. $$R^+ + Z^- \xrightarrow{\text{Fast}} R{-}Z$$

The order of reactivity of various alkyl halides through SN^2 mechanism is :

$$3° > 2° > 1°$$

The 3° alkyl halides are most reactive because the intermediate carbocation formed in their case is the most stable.

(*ii*) **SN^2 Mechanism** (*Bimolecular nucleophilic substitution*)

In this type the rate of reaction is dependent on the concentration of alkyl halide as well as nucleophile, *i.e.*,

$$\text{Rate} = k\,[RX]\,[Z^-]$$

Primary alkyl halides react by SN^2 mechanism via formation of a transition state

$$R{-}X + Z^- \longrightarrow \left[\overset{\delta-}{Z}\ldots\ldots R\ldots\ldots\overset{\delta-}{X}\right] \longrightarrow Z{-}R + \overset{-}{X}$$

Transition state

The order of reactivity of various alkyl halides through SN^2 mechanism is :

$$1° > 2° > 3°$$

Some of the nucleophilic reactions of haloalkanes are discussed below :

1. **Replacement by hydroxyl group** (*Formation of alcohols*). Haloalkanes on treatment with *aqueous solution* of KOH or *moist silver oxide* (Ag_2O/H_2O) give alcohols.

$$\underset{\text{Haloalkane}}{R{-}X} + :\overset{-}{O}H \longrightarrow \underset{\text{Alcohol}}{R{-}OH} + :\overset{-}{X}$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + \overset{+}{K}\overset{-}{O}H(aq) \longrightarrow \underset{\text{Ethanol}}{C_2H_5OH} + KBr$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + AgOH \xrightarrow[\text{Silver oxide}]{\text{Moist}} \underset{\text{Ethanol}}{C_2H_5OH} + AgBr$$

2. **Replacement by alkoxy group** (*Formation of ethers*). **(Williamson Synthesis)**

Haloalkanes on treatment with alcoholic sodium or potassium alkoxide form ethers.

$$\underset{\text{Haloalkane}}{R{-}X} + \underset{\text{Alkoxide ion}}{:\overset{-}{O}R'} \longrightarrow \underset{\text{Ether}}{R{-}O{-}R'} + :\overset{-}{X}$$

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$$\underset{\text{Bromoethane}}{C_2H_5Br} + \underset{\text{Sodium ethoxide}}{\overset{+}{Na} : \overset{-}{O}C_2H_5} \longrightarrow \underset{\text{Ethoxyethane}}{C_2H_5OC_2H_5} + NaBr$$

Ethers can also be prepared by heating alkyl halides with dry silver oxide, Ag_2O

$$\underset{\text{Bromoethane}}{2C_2H_5Br} + Ag_2O \xrightarrow{\text{heat}} \underset{\text{Ethoxyethane}}{C_2H_5—O—C_2H_5} + 2AgBr$$

For more details refer to Section 8.2.

3. **Replacement by cyano group** (*Formation of cyanides or nitriles*). Haloalkanes on treatment with alcoholic KCN solution give *alkanenitriles or alkyl cyanides* as the major product with a small amount of alkyl isocyanide.

$$\underset{\text{Haloalkane}}{R—X} + :\overset{-}{C}N \longrightarrow \underset{\text{Alkane nitrile}}{R—C \equiv N} + :\overset{-}{X}$$

$$\underset{\text{Iodoethane}}{CH_3—CH_2—I} + KCN \longrightarrow \underset{\text{Propane nitrile}}{CH_3—CH_2—C \equiv N} + KI$$

The alkyl cyanides so obtained can be used as starting materials for the preparation of a number of compounds.

(*i*) *Alkyl cyanides on* **partial hydrolysis** *with conc. HCl or alkaline solution of H_2O_2 give amides.*

$$CH_3—CH_2—C \equiv N + H_2O \xrightarrow[\text{Alkaline } H_2O_2]{\text{Conc. HCl or}} \underset{\text{Propanamide}}{CH_3—CH_2—\overset{O}{\overset{\|}{C}}—NH_2}$$

(*ii*) *On* **complete hydrolysis** *with dil. HCl, alkyl cyanides give carboxylic acids.*

$$CH_3—CH_2—C \equiv N + 2H_2O \xrightarrow{\text{dil. HCl}} \underset{\text{Propanoic acid}}{CH_3—CH_2—\overset{O}{\overset{\|}{C}}—OH} + NH_4Cl$$

(*iii*) *Alkyl cyanides on* **catalytic reduction** *with H_2/Ni or Na/ethyl alcohol* (**Mendius reaction**) *give primary amines.*

$$CH_3—CH_2—C \equiv N + 2H_2 \xrightarrow{\text{Ni}} \underset{\text{1-Aminopropane}}{CH_3—CH_2—CH_2—NH_2}$$

(*iv*) *Alkyl cyanides can also be reduced with $SnCl_2$ and HCl* (**Stephen reaction**) *to produce aldehydes.*

$$CH_3—CH_2—C \equiv N + 2[H] \xrightarrow[\text{HCl}]{SnCl_2} CH_3CH_2CH = NH \cdot HCl \xrightarrow[-NH_4Cl]{H_2O/H^+} \underset{\text{Propanal}}{CH_3CH_2CHO}$$

The reaction of alkyl halides with KCN gives us an important method for increasing the length of carbon chain by one carbon atom i.e., **ascending of series.**

4. **Replacement with isocyanide** (*Formation of isocyanides*). On reaction with alcoholic silver cyanide solution, haloalkanes give alkyl carbylamines or alkyl isocyanides as the major product alongwith a small amount of alkyl cyanide.

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$$R—X + alc.\ AgCN \longrightarrow \underset{\text{Isocyanide}}{R—NC} + AgX$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + alc.\ AgCN \longrightarrow \underset{\text{Ethyl carbylamine}}{C_2H_5NC} + AgBr$$

A curious question may aries here in the mind of the reader as to why reaction of alkyl halides with KCN produces cyanide whereas the reaction with AgCN gives isocyanide as the product. For details refer to Section 9.6.

5. **Replacement by amino group** (*Formation of amines*). On heating haloalkane with alcoholic ammonia solution in a sealed tube at 383 K, halogen is replaced by $—NH_2$ group to form primary amine.

$$\underset{\text{Haloalkanes}}{R—X} + \ddot{N}H_3\ (alc.) \longrightarrow \underset{\substack{\text{Primary amine}\\(1^\circ)}}{R—\ddot{N}H_2} + HX$$

$$\underset{\text{Bromoethane}}{C_2H_5—Br} + \ddot{N}H_3\ (alc.) \longrightarrow \underset{\text{Aminoethane}}{C_2H_5—\ddot{N}H_2} + HBr$$

In case haloalkane is in excess, the other two hydrogen atoms of amino group are also replaced by alkyl groups leading to the formation of *secondary* and *tertiary amines*.

$$\underset{\text{Bromoethane}}{C_2H_5—Br} + \underset{\text{Ethyl amine}}{H\ddot{N}HC_2H_5} \longrightarrow \underset{\substack{\text{Diethyl amine}\\\text{(N-Ethylamino)}\\\text{ethane)}}}{(C_2H_5)_2\ddot{N}H} + HBr$$

$$\underset{\text{Diethylamine}}{(C_2H_5)_2NH} + \underset{\text{Bromoethane}}{Br—C_2H_5} \longrightarrow \underset{\substack{\text{Triethyl amine}\\\text{(N, N-Diethyl}\\\text{aminoethane)}}}{(C_2H_5)_3\ddot{N}} + HBr$$

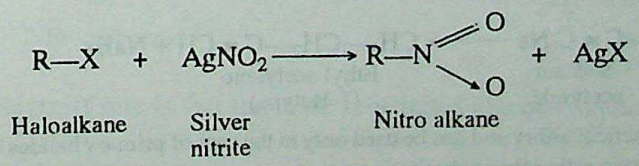
Tertiary amine so formed can further combine with another molecule of alkyl halide to give quaternary ammonium salt as the product.

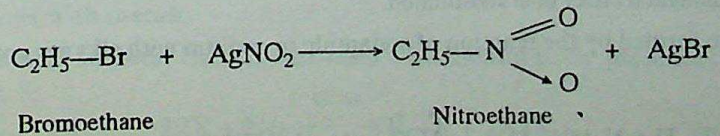
$$C_2H_5—Br + \underset{\text{Triethyl amine}}{(C_2H_5)_3\ddot{N}} \longrightarrow \underset{\substack{\text{Tetraethyl}\\\text{ammonium bromide}}}{[(C_2H_5)_4\overset{+}{N}]\overset{-}{Br}}$$

This reaction is known as **Hoffmann ammonolysis** of alkyl halides.

6. **Replacement by nitro group** (*Formation of nitroalkane*). On treating ethanolic solution of haloalkanes with silver nitrite (Ag—O—N = O), nitro alkane is formed.

It is because the bond between Ag—O being covalent, the lone pair on nitrogen acts as attacking site for nucleophilic substitution.





7. **Replacement by nitrite group** (*Formation of alkyl nitrites*). On treating haloalkanes with potassium nitrite *alkyl nitrite* is formed. *It is because bond between K—O is ionic in nature therefore negative charge on oxygen serves an attacking site.* For details refer to Section 9.10.

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$$\underset{\text{Haloalkane}}{R—X} + KNO_2 \longrightarrow \underset{\text{Alkyl nitrite}}{R—O—N=O} + KX$$

$$\underset{\text{Bromoethane}}{C_2H_5—Br} + KNO_2 \longrightarrow \underset{\text{Ethyl nitrite}}{C_2H_5—O—N=O} + KBr$$

8. **Replacement by —SH (Hydro sulphide) group** (*Formation of thiols or mercaptans*). On treating haloalkane with $\overset{+\,-}{KSH}$ (potassium hydrogen sulphide) or $\overset{+\,-}{NaSH}$ (sodium hydrogen sulphide) *thioalcohols* are formed.

$$\underset{\text{Haloalkane}}{R—X} + :\overset{-}{S}H \longrightarrow \underset{\text{Thioalcohol}}{R—SH} + :\overset{-}{X}$$

$$C_2H_5—Br + \overset{+\,-}{KSH} \longrightarrow \underset{\substack{\text{Ethyl thioalcohol}\\ \text{(Ethanethiol)}}}{C_2H_5—SH} + KBr$$

9. **Replacement of halogen by mercaptide (: SR′) group** (*Formation of thioether*). On treating haloalkanes with sodium mercaptide **thioethers** are formed.

$$\underset{\text{Haloalkane}}{R—X} + \underset{\text{Mercaptide ion}}{:\overset{-}{S}R} \longrightarrow \underset{\text{Thioether}}{R—S—R} + :\overset{-}{X}$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + \underset{\substack{\text{Sod. methyl}\\ \text{mercaptide}}}{\overset{+\,-}{NaSCH_3}} \longrightarrow \underset{\substack{\text{Ethylmethyl sulphide}\\ \text{(Ethylmethylthioether)}}}{C_2H_5SCH_3} + NaBr$$

Thioethers can also be obtained by reaction of alkyl halides with sodium or potassium sulphide

$$\left.\begin{matrix} R— X \\ R— X \end{matrix}\right\} + Na_2S \longrightarrow R_2S + 2NaX$$

10. **Replacement by alkynyl group** (*Formation of higher alkynes*). On treating haloalkanes with sodium alkynide ($RC\equiv\overset{-\,+}{C}Na$), *higher alkynes* are formed. *The reaction can thus be employed for* **ascending of series.**

$$R—X + \underset{\text{Sodium acetylide}}{HC\equiv\overset{-\,+}{C}Na} \longrightarrow \underset{\text{Alkyl acetylene}}{R—C\equiv CH} + NaX$$

$$CH_3—CH_2—Br + H—C\equiv\overset{-\,+}{C}Na \longrightarrow \underset{\substack{\text{Ethyl acetylene}\\ \text{(1-Butyne)}}}{CH_3—CH_2—C\equiv CH} + NaBr$$

Sodium acetylide

The reaction is of limited practical utility and can be used only in the case of primary halides because the secondary and tertiary halides undergo elimination rather than substitution.

Sodium alkynides are formed by the reaction of sodamide or sodium with alkynes containing terminal triple bond.

$$H—C\equiv C—H + \underset{\text{Sodaminde}}{NaNH_2} \longrightarrow \underset{\text{Sod. acetylide}}{\overset{+\,-}{NaC}\equiv C—H} + NH_3$$

11. **Replacement by carboxylate group** (*Formation of carboxylic esters*). Haloalkanes on treatment with silver salt of carboxylic acid in ethanol give *esters*.

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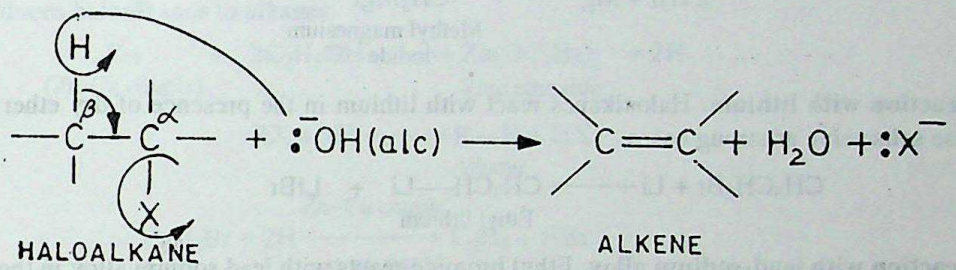
$$\underset{\text{Haloalkanes}}{R{-}X} + R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O^{-}: \longrightarrow \underset{\text{Ester}}{R'{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}O{-}R} + :\overset{-}{X}$$

$$C_2H_5Br + CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}\overset{-}{O}\overset{+}{A}g \longrightarrow CH_3{-}\overset{\overset{\displaystyle O}{\|}}{C}{-}OC_2H_5 + AgBr$$

Silver acetate — Ethyl acetate

II. Dehydrohalogenation reactions or β-Elimination reactions

When haloalkanes are heated with alcoholic KOH, they undergo dehydrohalogenation to form alkenes. These reactions are called β-eliminations because the hydrogen atom present at β position of the haloalkane is removed.



$$CH_3{-}CH_2{-}Br + KOH\ (alc.) \longrightarrow H_2C = CH_2 + KBr + H_2O$$

Bromoethane — Ethene

The **reactivity** *of haloalkanes towards elimination reaction follows the order*

tertiary > secondary > primary

This can be explained on the basis of the stability of the alkene formed after dehydrohalogenation. Tertiary alkyl halides on dehydrohalogenation form most substituted alkenes, which being more stable are formed at faster rate. On the other hand primary alkyl halides yield least substituted alkenes, which being less stable are formed at slower rate.

In case the haloalkanes can eliminate hydrogen halide in two different ways, the preferred alkene is the one which is maximum alkylated i.e., which carries more number of alkyl groups attached to the doubly bonded carbon atoms. This generalisation is known as **Saytzeff Rule**. For example,

$$\underset{\text{2-Bromobutane}}{CH_3{-}\overset{\beta}{C}H_2{-}\overset{\alpha}{C}H(Br){-}\overset{\beta}{C}H_3} \xrightarrow{\text{alc. KOH}} \begin{cases} \underset{\substack{\text{2-Butene}\\ \text{major (80\%)}}}{CH_3{-}CH = CH{-}CH_3} \\ \underset{\substack{\text{1-Butene}\\ \text{minor (20\%)}}}{CH_3{-}CH_2{-}CH = CH_2} \end{cases}$$

The basis of Saytzeff rule is that the more substituted alkene is more stable and hence is formed at faster rate.

III. Reactions with metals

1. **Reaction with sodium.** Haloalkanes react with sodium in the presence of ether to form alkanes.

$$2RX + 2Na \xrightarrow{\text{ether}} R{-}R + 2NaX$$

$$2CH_3I + 2Na \xrightarrow{\text{ether}} \underset{\text{Ethane}}{CH_3{-}CH_3} + 2NaI$$

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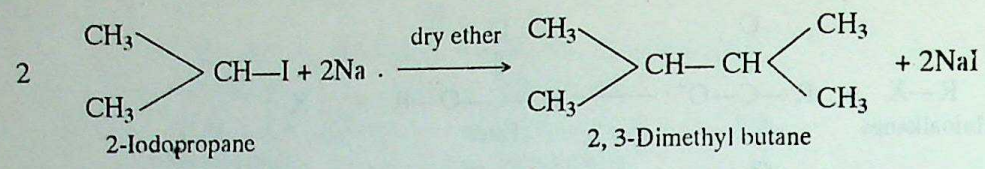


This reaction is known as **Wurtz reaction** and ***is generally applied to prepare symmetrical alkanes with more number of carbon atoms*** **(ascending of series)**. The tertiary halides do not undergo this reaction.

2. **Reaction with magnesium.** Haloalkanes react with magnesium in the presence of dry ether to form alkyl magnesium halides (**Grignard reagents**).

$$RX + Mg \xrightarrow{\text{dry ether}} RMgX$$

$$CH_3I + Mg \longrightarrow \underset{\text{Methyl magnesium iodide}}{CH_3MgI}$$

3. **Reaction with lithium.** Haloalkanes react with lithium in the presence of dry ether to for alkyl lithium. These salts serve as strong bases.

$$CH_3CH_2Br + Li \longrightarrow \underset{\text{Ethyl lithium}}{CH_3CH_2—Li} + LiBr$$

4. **Reaction with lead-sodium alloy.** Ethyl bromide reacts with lead sodium alloy in the presence of dry ether to form tetraethyl lead (TEL), the well known antiknock agent.

$$4CH_3CH_2Br + 4Pb(Na) \longrightarrow (CH_3CH_2)_4Pb + 4NaBr + 3Pb.$$

Coupling of Alkyl halides with Organometallic Compounds

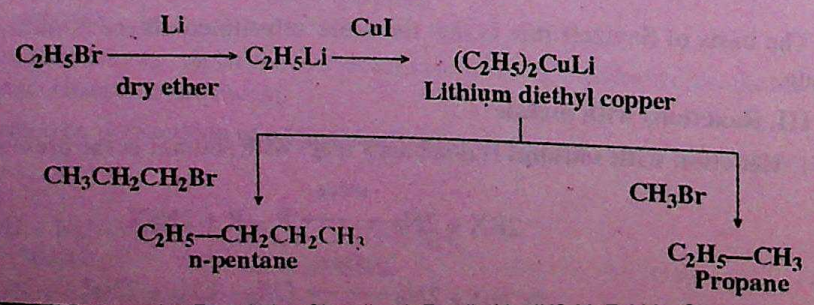
This method was developed by E.J. Corey and Herbert House to prepare alkanes with higher number of carbon atoms. In this method lithium dialkyl copper, R_2CuLi is reacted with an alkyl halide.

$$\underset{\text{Lithium dialkyl copper}}{R—\overset{R}{\overset{|}{C}}uLi} + R'—X \longrightarrow \underset{\text{Alkane}}{R—R'} + RCu + LiX$$

Lithium dialkyl copper is prepared by the reaction of alkyl lithium with cuprous halide, CuX.

$$2R—Li + CuX \longrightarrow R—\overset{R}{\overset{|}{C}}uLi + LiX$$

For good yield, the alkyl halide should preferrably be primary while the alkyl group in the R_2CuLi may be primary, secondary or tertiary. For example,



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IV. Reduction

Haloalkanes can be reduced to alkanes by any of the following methods :

1. **Reaction with H_2/Ni.** Haloalkanes on reaction with hydrogen in the presence of nickel or palladium as catalyst give alkanes.

$$R—X + H_2 \xrightarrow[525\ K]{Ni} R—H + HX$$

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + H_2 \xrightarrow[525\ K]{Ni} \underset{\text{Ethane}}{C_2H_6} + HBr$$

2. **Reaction with zinc-copper couple.** In the presence of alcohols (95% ethyl alcohol), zinc-copper couple reduces haloalkanes to alkanes.

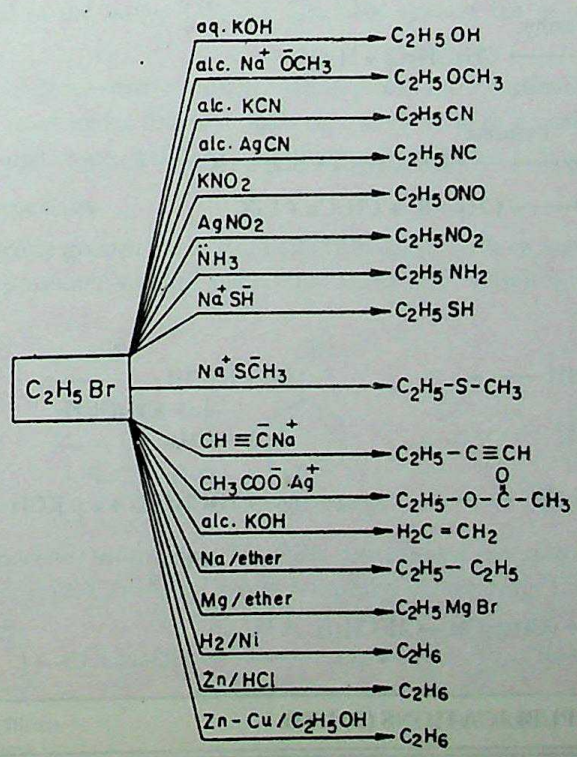
$$\underset{\text{(Zn-Cu couple)}}{Zn} + 2C_2H_5OH \longrightarrow \underset{\text{Zinc ethoxide}}{Zn(OC_2H_5)_2} + 2H$$

$$RX + 2H \longrightarrow \underset{\text{Alkane}}{R—H} + HX$$

$$C_2H_5Br + 2H \xrightarrow[C_2H_5OH]{\text{Zn–Cu couple}} C_2H_6 + HBr$$

Similarly, Zn/HCl, Zn/NaOH, Na/C_2H_5OH, Sn/HCl or HI/red P at 430 K can also reduce haloalkanes to alkanes.

The **summary** of different reactions of alkyl halides is given below :



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REVIEW PROBLEMS

7.15. Which isomer of C_4H_9Cl will have the lowest boiling point ?

7.16. Arrange the following in order of increasing reactivity towards nucleophilic substitution :

(*i*) $(CH_3)_2CHBr$ (*ii*) $(CH_3)_2CHI$ (*iii*) $(CH_3)_2CHCl$.

7.17. Which reagent will convert CH_3Br to propyne ?

7.18. Name the alkyl halide which can give ethane as well as methane in single steps.

7.19. Which product will form when optically active halide with formula C_4H_9Br is subjected to dehydrohalogenation ?

7.20. Name the reagent that can be used to convert ethyl bromide to ethyl propionate.

7.21. Which metal is used in the preparation of Grignard's reagent from alkyl halides ?

7.22. Which isomer of C_4H_9Cl will have the lowest reactivity towards substitution reactions ?

7.23. Name the reagents used to convert

(*i*) Propene to allyl bromide (*ii*) Ethyl chloride to ethoxy ethane

(*iii*) Silver isobutyrate to sec-propyl bromide (*iv*) Methyl iodide to 2-Butyne

(*v*) Chlorobenzene to toluene.

7.24. Name the following reactions :

(*i*) $C_6H_5N_2^+Cl^- + HBF_4 \longrightarrow C_6H_5F + BF_3 + HCl$

(*ii*) $2CH_3COOAg + I_2 \xrightarrow{CCl_4} CH_3COOCH_3 + 2AgI$

(*iii*) $CH_3CH_2OH + HCl \xrightarrow[ZnCl_2]{anhy.} CH_3CH_2Cl + H_2O$

(*iv*) $CH_3CH_2OH + SOCl_2 \xrightarrow{Pyridine} CH_3CH_2Cl + SO_2 + HCl$

(*v*) $CH_3-\underset{\underset{CH_3}{|}}{CuLi} + R'X \longrightarrow CH_3-R' + CH_3Cu + LiX.$

7.25. Complete the following :

(*i*) $CH_3I + (CH_3CH_2)_2NH \longrightarrow$

(*ii*) $CH_3\underset{\underset{CH_3}{|}}{CHI} \xrightarrow[CH_3OCH_3]{Na}$

(*iii*) $CH_3CH_2Cl + \overset{+}{Na}C \equiv CH \longrightarrow$

(*iv*) $CH_3\underset{\underset{Cl}{|}}{CH}CH_3 + \text{aq. KOH} \longrightarrow$

(*v*) $? \xrightarrow[ZnCl_2]{HCl} ? \xrightarrow[\text{dry ether}]{Na} (CH_3)_2CH-CH(CH_3)_2.$

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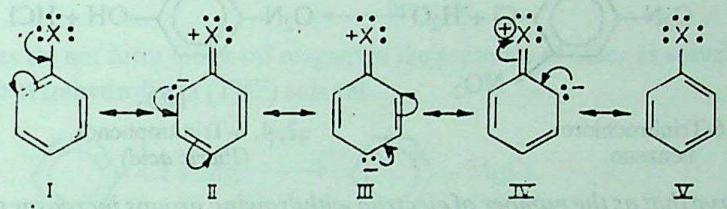
REACTIONS OF HALOARENES

Haloarenes are much less reactive towards nucleophilic substitution reactions than haloalkanes. The less reactivity of haloarenes can be explained as follows :

(*i*) **Withdrawal of electrons by benzene and stabilization by resonance.** In haloarenes, the electron pair of halogen atom is in conjugation with π electrons of benzene ring. Thus, halobenzene is a resonance hybrid of the following structures :



The contributing structures II, III and IV indicate that C—X bond has partial double bond character.

As a result the C—X bond in halobenzene is shorter and hence, stronger as compared to that in alkyl halides. Thus, cleavage of C—X bond in halobenzene becomes difficult which makes it less reactive towards nucleophilic substitution.

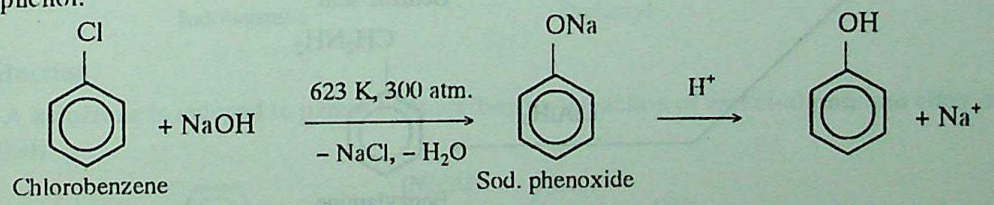
(*ii*) **Different hybrid state of carbon atom.** In haloalkanes, the carbon atom bearing halogen is sp^3 hybridized while halogen bearing carbon atom is sp^2 hybridized in haloarenes. The sp^2 hybrid carbon is more electronegative and hence holds the electron pair more firmly as compared to sp^3 hybridized carbon. Therefore, C—X bond of haloalkanes is cleaved more easily than in haloarenes.

(*iii*) **Polarity of C—X bond.** The C—X bond in haloalkanes is more polar than the C—X bond in haloarenes. (This is supported by dipole moment of these bonds. Dipole moment of chloro benzene is 1.7 D whereas that of haloalkanes fall in the range 2.0—2.2 D). Now greater the polarity of bond more is the reactivity.

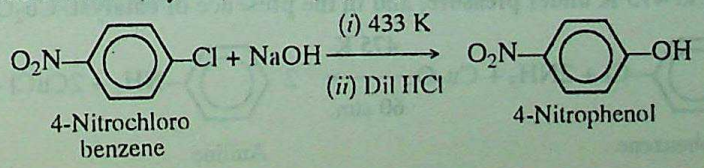
Thus, *haloarenes are much less reactive towards nucleophilic substitution reactions* than haloalkanes. However, they can be made to react under drastic conditions, such as high pressure and high temperature. Some of the characteristic reactions of aryl halides or halobenzene are given below :

I. Nucleophilic Substitution Reactions

1. **Replacement by hydroxy group.** On heating chlorobenzene with an aqueous solution of NaOH at 623 K under 300 atmosphere pressure, sodium phenoxide is formed which on subsequent acidification produces phenol.



The reactivity of the haloarenes towards nucleophilic substitution reaction increases if some electron withdrawing group such as nitro, cyano, carboxyl group is attached to the ring. For example,



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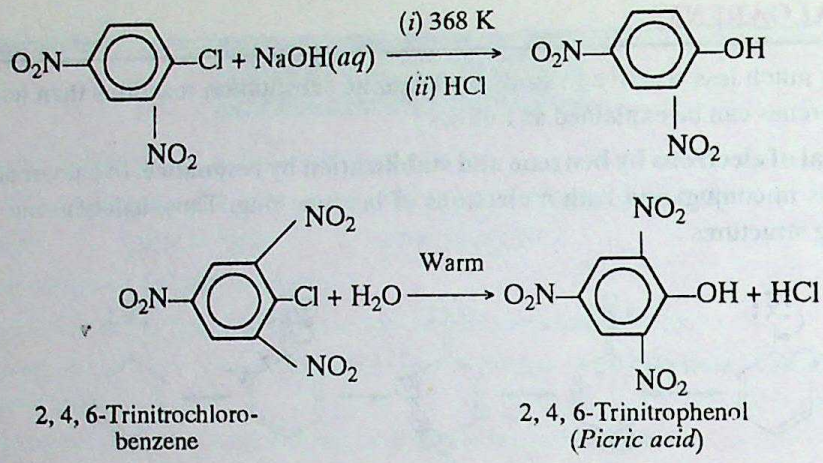
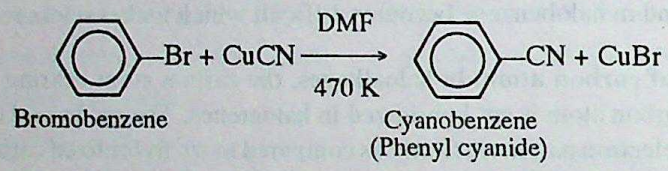
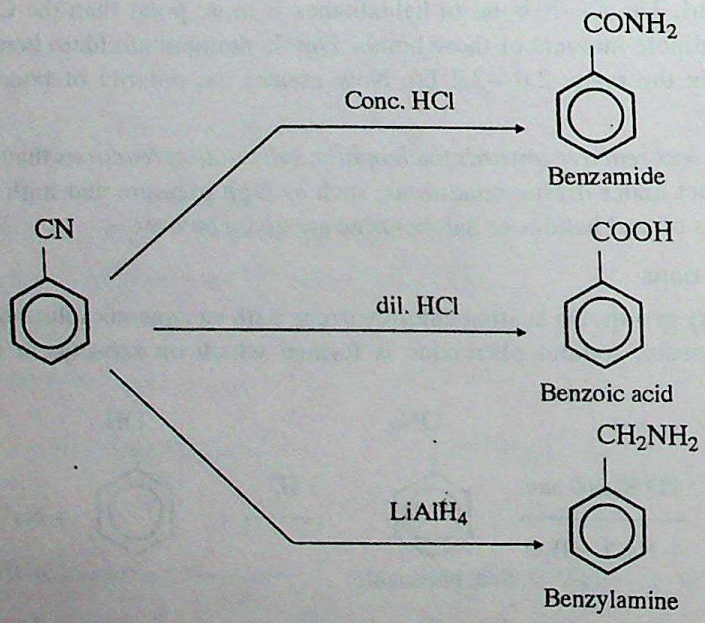


Thus, we observe that as the number of electron withdrawing groups increases the reactivity increases.

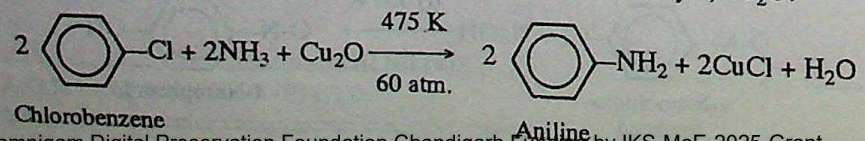
2. **Replacement by cyano group.** When heated with anhydrous CuCN in the presence of pyridine or dimethyl formamide (DMF) at 470 K, bromobenzene gives cyanobenzene.



The resulting cyanide can be employed for the preparation of a number of compounds.



3. **Replacement by amino group.** Halogen atom of haloarenes is replaced by amino group by reacting it with aqueous ammonia at 475 K under pressure, and in the presence of catalyst, Cu_2O.



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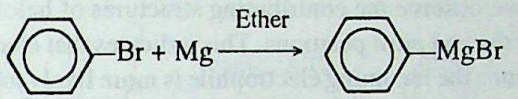
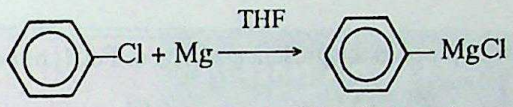
II. Reactions with Metals

1. **Action with magnesium.** Aryl bromides and iodides form Grignard's reagent with magnesium in dry ether.



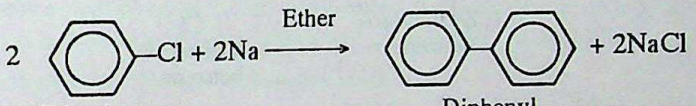
Bromobenzene — Phenyl magnesium bromide

Aryl chlorides do not form Grignard reagent in the presence of ether as solvent. However, these form Grignard's reagent in tetrahydrofuran (THF) solvent.



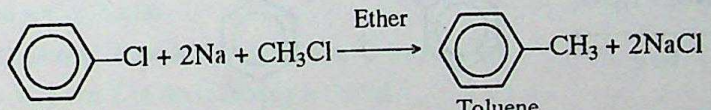
Chlorobenzene — Phenyl magnesium chloride

2. **Reaction with sodium.** Haloarenes react with sodium in the presence of ether. During reaction two phenyl rings unite. This reaction is called **Fittig reaction.**



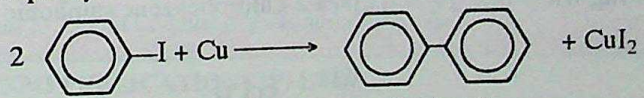
Chlorobenzene — Diphenyl

However, aryl halides when treated with haloalkane and sodium in dry ether undergo **Wurtz Fittig reaction.**



Chlorobenzene — Toluene

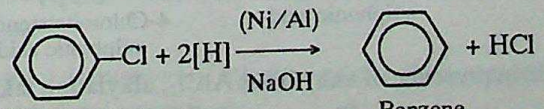
3. **Reaction with copper powder** (*Ulmann reaction*). Iodobenzene when heated with copper powder in a sealed tube gives diphenyl.



Iodobenzene — Diphenyl

III. Reduction

A haloarene is reduced to parent hydrocarbon by the action of nickel-aluminium alloy in the presence of an alkali.



Chlorobenzene — Benzene

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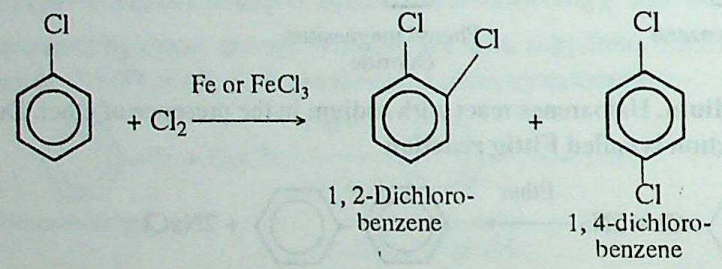
IV. Ring Substitution Reactions

Haloarenes undergo electrophilic substitution reactions in the benzene ring. ***The presence of halogen atom in the ring directs the incoming substituent to ortho and para positions.*** The *ortho, para* directing effect of halogen atom can be understood if we observe the contributing structures of halobenzene. In structures II, III and IV there is negative charge at *ortho* and *para* positions. This indicates that electron density is relatively more at ortho and para positions and hence the incoming electrophile is more likely to attack on these positions resulting in the formation of ortho and para substituted products.

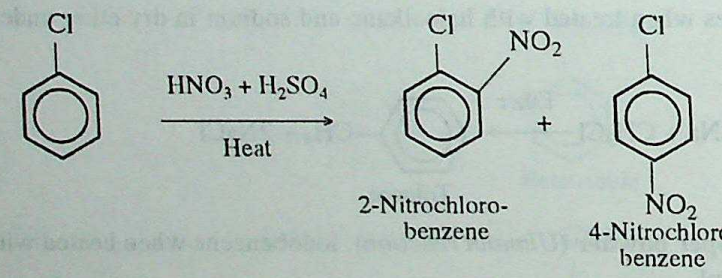
Haloarenes are less reactive than benzene towards electrophilic substitution reactions.

This is due to the reason that halogen atom because of its electron withdrawing inductive effect decreases the electron density at the benzene ring. Some ring substitution reactions of haloarenes are given below :

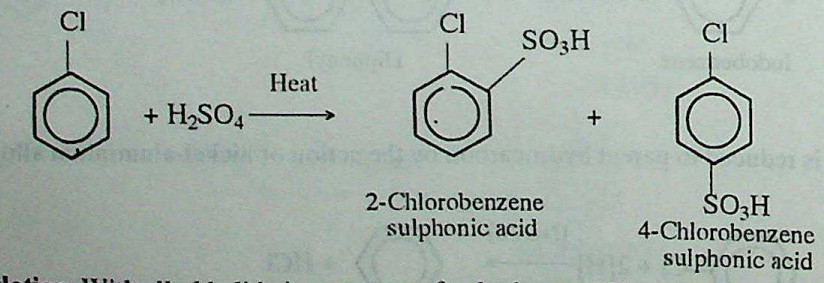
1. **Halogenation.** Halogenation takes place in the presence of iron or $FeCl_3$ or anhy. $AlCl_3$ as a catalyst.



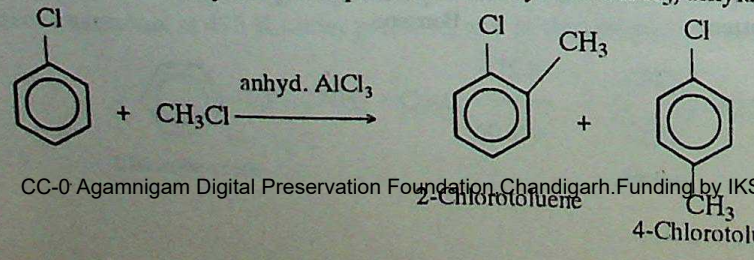
2. **Nitration.** Nitration is carried out with conc. HNO_3 and conc. H_2SO_4.



3. **Sulphonation.** Heating with conc. H_2SO_4 gives 2-chlorobenzene sulphonic acid and 4-chlorobenzene sulphonic acid.



4. **Alkylation.** With alkyl halide in presence of anhydrous $AlCl_3$, alkylation takes place. For example,



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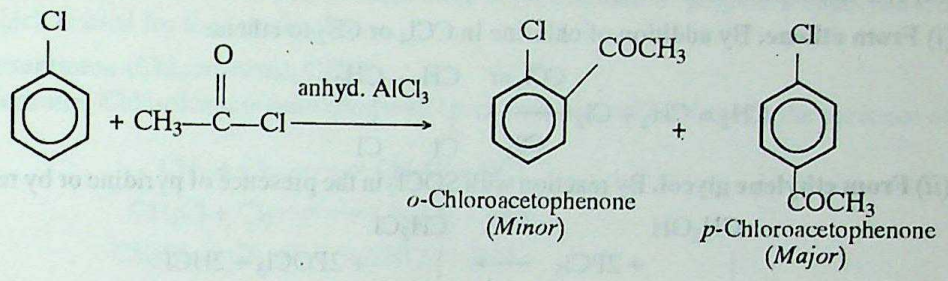
5. **Acylation.** Acylation of haloarenes can be carried out with the reaction of acyl chlorides in the presence of anhydrous $AlCl_3$. For example,



REVIEW PROBLEMS

7.26. Which reagents are required for the one step conversion of chlorobenzene into toluene. Also name the reaction.

7.27. Which out of *o*-chloronitro benzene and 2, 4, 6-trinitrochlorobenzene is more reactive towards nucleophilic substitution ?

7.28. Two compounds *o*-chlorobenzyl iodide and *p*-iodobenzyl chloride were separately treated with aqueous KOH. $AgNO_3$ solution is then added to each which will give yellow ppt. and why ?

7.29. What are the reagents involved in the Ulmann reaction ?

7.30. Out of various possible isomers of C_7H_7Cl containing benzene ring suggest the structure with weakest C—Cl bond.

7.31. Give the structure of 4, 4-Diiodobiphenyl.

7.32. Name an aralkyl halide.

7.33. What is diphenyl. How is it prepared from chlorobenzene ?

7.34. Identity X, Y and Z in the following reactions :

$$(i)\ C_6H_6 \xrightarrow[AlCl_3]{CH_3COCl} X \xrightarrow{LiAlH_4} Y \xrightarrow{\text{anhy. } AlCl_3} Z \quad (ii)\ C_6H_5Cl \xrightarrow[Cu_2O]{NH_3} X \xrightarrow[NaNO_2 \text{ and } HCl]{} Y \xrightarrow[\text{Warm}]{KI} Z.$$

7.35. How will you obtain 2, 2′-dinitrodiphenyl from chloro benzene ?

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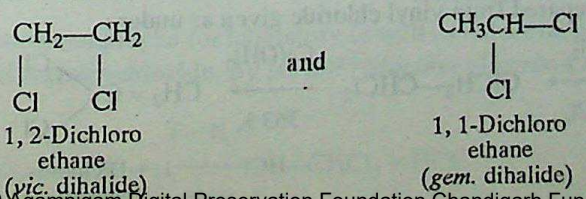
7.8. POLYHALOGEN COMPOUNDS

The carbon compounds containing more than one halogen atom in their molecules are known as polyhalogen compounds. Some common polyhalogen compounds are briefly discussed below :

1. Dichloroethanes

These are substitution derivatives of ethane in which the two hydrogen atoms are replaced by chlorine atoms. The two possible structural isomers are :



1, 2-Dichloro ethane (*vic.* dihalide) — 1, 1-Dichloro ethane (*gem.* dihalide)

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Preparation

(A) *1, 2-Dichloroethane* can be obtained by the following reactions :

(*i*) **From ethene.** By addition of chlorine in CCl_4 or CS_2 to ethene

$$CH_2 = CH_2 + Cl_2 \xrightarrow[CS_2]{CCl_4 \text{ or}} \begin{array}{c} CH_2 — CH_2 \\ | \qquad | \\ Cl \qquad Cl \end{array}$$

(*ii*) **From ethylene glycol.** By reaction with $SOCl_2$ in the presence of pyridine or by reaction with PCl_5.

$$\underset{\text{1, 2-Ethanediol}}{\begin{array}{c} CH_2OH \\ | \\ CH_2OH \end{array}} + 2PCl_5 \longrightarrow \underset{\text{1, 2-Dichloroethane}}{\begin{array}{c} CH_2Cl \\ | \\ CH_2Cl \end{array}} + 2POCl_3 + 2HCl$$

(B) *1, 1-Dichloroethane* can be prepared as follows :

(*i*) **From ethanal.** By reaction with PCl_5

$$CH_3CHO + PCl_5 \longrightarrow CH_3CHCl_2 + POCl_3$$

(*ii*) **From acetylene.** By addition of HCl

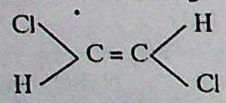
$$HC \equiv CH + HCl \longrightarrow \underset{\text{Vinyl chloride}}{CH_2 = CH — Cl} \xrightarrow[\text{M. Rule}]{HCl} \underset{\text{1, 1-Dichloroethane}}{CH_3CHCl_2}$$

2. Dichloroethenes

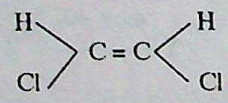
These are substitution derivatives of ethene in which two hydrogen atoms of ethene are replaced by chlorine atoms. Two structural isomers are possible for dichloroethene. These are

$$\underset{\substack{\text{1, 2-Dichloroethene} \\ \text{(Acetylene dichloride)}}}{ClCH = CHCl} \quad \text{and} \quad \underset{\substack{\text{1, 1-Dichloroethene} \\ \text{(Vinylidene dichloride)}}}{CH_2 = CCl_2}$$

1, 2-Dichloroethene can exhibit geometric isomerism



trans-1, 2-Dichloroethene



cis-1, 2-Dichloroethene

Preparation

(A) *1, 2-Dichloroethene* is prepared by the following reactions :

(*i*) **From Westron.** By the action of zinc on westron (1, 1, 2, 2-tetrachloroethane).

$$\underset{\substack{\text{1, 1, 2, 2-Tetrachloro-} \\ \text{ethane}}}{Cl_2CH — CHCl_2} + Zn \longrightarrow \underset{\substack{\text{1, 2-Dichloro-} \\ \text{ethene}}}{ClCH = CHCl} + ZnCl_2$$

(*ii*) It can also be obtained by the addition of chlorine in CCl_4 to acetylene.

$$HC \equiv CH + Cl_2 \xrightarrow{CCl_4} ClCH = CHCl$$

(B) *1, 1-Dichloroethene* is prepared from vinyl chloride given as under :

$$\underset{\text{Vinyl chloride}}{CH_2 = CH — Cl} \xrightarrow[CCl_4]{Cl_2} ClCH_2 — CHCl_2 \xrightarrow[\text{363 K}]{Ca(OH)_2} CH_2 = C\begin{array}{l} Cl \\ Cl \end{array}$$

$$-HCl \qquad \text{1, 1-Dichloro-ethene}$$

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Uses 1. As solvent for rubber.

2. Vinylidene dichloride is polymerized with vinyl chloride to prepare a copolymer, ***saran***, which is used for food packaging.

3. Trichloromethane (Chloroform), $CHCl_3$

(*i*) **From Methane.** Chloroform is ***manufactured*** by chlorination of methane in the presence of light or catalysts.

$$CH_4 + Cl_2 \longrightarrow CH_3Cl + HCl$$

$$CH_3Cl + Cl_2 \longrightarrow CH_2Cl_2 + HCl$$

$$CH_2Cl_2 + Cl_2 \longrightarrow CHCl_3 + HCl$$

$$CHCl_3 + Cl_2 \longrightarrow CCl_4 + HCl$$

The mixture of CH_3Cl, CH_2Cl_2, $CHCl_3$ and CCl_4 can be separated by fractional distillation.

(*ii*) **From Chloral hydrate.** ***Pure chloroform*** can be obtained by distilling chloral or chloral hydrate with concentrated aqueous NaOH solution or KOH solution.

$$NaOH + \underset{\text{Chloral}}{CCl_3CHO} \longrightarrow HCOONa + CHCl_3$$

$$NaOH + \underset{\text{Chloral hydrate}}{CCl_3CH(OH)_2} \longrightarrow HCOONa + \underset{\text{Chloroform}}{CHCl_3} + H_2O$$

(*iii*) **Laboratory Method.** In this method chloroform is obtained ***from ethanol or acetone by reaction with a paste of bleaching powder and water.***

In this reaction, bleaching powder serves as a source of chlorine which first oxidises ethanol to acetaldehyde, which is then further chlorinated to chloral. Chloral reacts with $Ca(OH)_2$ given by $CaOCl_2$ to give chloroform and calcium formate.

(*a*) ***In case of ethanol, the reaction occurs as follows***

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$CH_3CH_2OH + Cl_2 \xrightarrow{\text{Oxidation}} CH_3CHO + 2HCl$$

$$CH_3CHO + 3Cl_2 \xrightarrow{\text{Chlorination}} \underset{\text{Chloral}}{CCl_3CHO} + 3HCl$$

$$Ca(OH)_2 + 2CCl_3CHO \xrightarrow{\text{Hydrolysis}} \underset{\text{Chloroform}}{2CHCl_3} + \underset{\text{Calcium formate}}{(HCOO)_2Ca}$$

(*b*) ***In case of acetone, the reaction takes place as given below.***

$$CaOCl_2 + H_2O \longrightarrow Ca(OH)_2 + Cl_2$$

$$CH_3COCH_3 + 3Cl_2 \xrightarrow{\text{Chlorination}} \underset{\text{Trichloroacetone}}{CCl_3COCH_3}$$

$$Ca(OH)_2 + CCl_3COCH_3 \xrightarrow{\text{Hydrolysis}} CHCl_3 + \underset{\text{Calcium acetate}}{(CH_3COO)_2Ca}$$

This method can be employed for laboratory as well as industrial preparation of chloroform.

(*iv*) **From Carbontetrachloride.** *By partial reduction of carbon tetrachloride with iron filings and water:*

$$CCl_4 + 2[H] \xrightarrow[\text{Heat}]{Fe/H_2O} CHCl_3 + HCl$$

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Chloroform manufactured by this method is used as a solvent as it is not of required purity for its use as an anaesthetic agent.

Physical Properties

Chloroform is a colourless, heavy liquid which has sweetish sickly odour and taste. It boils at 334 K and is slightly soluble in water. It is heavier than water. As inhaling of the vapours of chloroform induces unconsciousness therefore it can be used as an anaesthetic agent for surgery.

Chemical Properties

1. Action of sun light and air. In presence of sun light chloroform is oxidized by air to produce a highly poisonous compound phosgene, $COCl_2$.

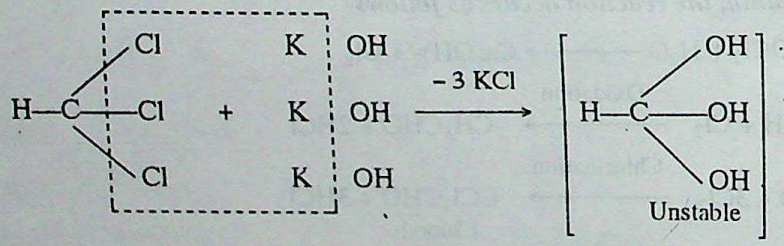
$$2CHCl_3 + O_2 \xrightarrow{\text{Sun light}} 2COCl_2 + 2HCl$$

As chloroform is used for anaesthetic purposes therefore in order to maintain a high purity of chloroform this reaction can be avoided by storing it in dark bottles, completely filled upto brim. *The use of dark bottles (brown or blue) cuts off active light radiations and filling upto brim keeps out air.* Apart from this a small amount of enthanol (1%) is usually added to bottles of chloroform. *Addition of a little ethanol fixes the toxic $COCl_2$ as non-poisonous diethyl carbonate.*

$$COCl_2 + 2C_2H_5OH \longrightarrow O{=}C\begin{matrix} OC_2H_5 \\ OC_2H_5 \end{matrix} + 2HCl$$

Diethyl carbonate

2. Hydrolysis. When boiled with aqueous KOH, chloroform is hydrolysed to potassium formate.



$$\xrightarrow{-H_2O} H{-}\overset{\overset{O}{\|}}{C}{-}OH \xrightarrow[-H_2O]{+KOH} HCOOK$$

Potassium formate

3. Reduction. Chloroform can be reduced to methylene chloride with zinc and HCl.

$$Zn + 2HCl \longrightarrow ZnCl_2 + 2[H]$$

$$CHCl_3 + 2[H] \longrightarrow CH_2Cl_2 + HCl$$

Dichloromethane (Methylene chloride)

However, on reduction with zinc and water (neutral medium) methane is obtained.

$$CHCl_3 \xrightarrow{Zn + H_2O} CH_4 + 3HCl$$

4. Reaction with acetone. Chloroform reacts with acetone in the presence of a base such as KOH and forms the addition product, *chloretone.*

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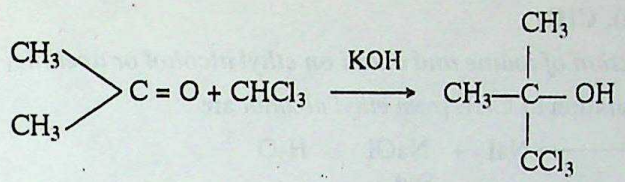


Acetone Chloretone

Chloretone is used as hypnotic (a sleep inducing) drug.

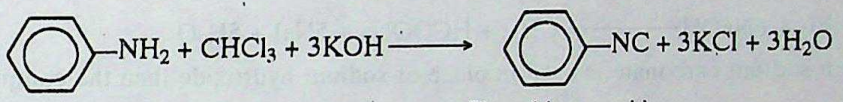
5. Reaction with nitric acid. Chloroform reacts with conc. HNO_3 on heating.

$$CHCl_3 + HONO_2 \longrightarrow CCl_3 . NO_2 + H_2O$$

Chloropicrin

Chloropicrin is used as an insecticide and war gas.

6. Reaction with primary amines. (*Carbylamine reaction*). When chloroform is warmed with a primary amine (aliphatic or aromatic) in the presence of alcoholic KOH, an offensive smell of *isocyanide* or *carbylamine* is obtained.



Aniline Phenyl iso-cyanide

This is the *isocyanide test* and employed for the detection of primary amines.

7. Reaction with sliver powder. On heating with silver powder, chloroform forms acetylene.

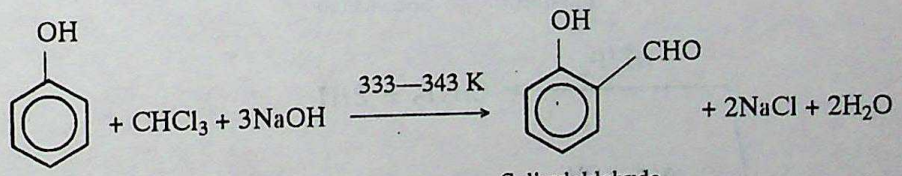
$$2CHCl_3 + 6Ag \xrightarrow{\text{Heat}} CH \equiv CH + 6AgCl$$

Acetylene

8. Chlorination. On further chlorination it gives CCl_4.

$$CHCl_3 + Cl_2 \xrightarrow{h\nu} CCl_4 + HCl$$

9. Reimer-Tiemann reaction. Chloroform reacts with phenol and alc. KOH to form salicylaldehyde.



Phenol Salicylaldehyde (2-Hydroxybenzaldehyde)

10. Reaction with Silver nitrate. Chloroform does not produce a precipitate when treated with aqueous $AgNO_3$. *It is because the C—Cl bond in chloroform is covalent and does not ionise in aqueous solution to produce chloride ions.*

Uses of Chloroform

1. As solvent in oils and varnishes.
2. In medicines such as cough syrups.
3. As preservative for anatomical specimens.
4. As laboratory reagent.
5. As an anaesthetic.

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4. Triiodomethane (Iodoform), CHI_3

Iodoform is prepared by the action of iodine and alkali on ethyl alcohol or acetone.

Reactions involved in the preparation of CHI_3 *from ethyl alcohol* are :

$$2NaOH + I_2 \longrightarrow NaI + \underset{\text{Sod. hypoiodite}}{NaOI} + H_2O$$

$$C_2H_5OH + NaOI \xrightarrow{\text{Oxidation}} CH_3CHO + NaI + H_2O$$

$$CH_3CHO + 3NaOI \xrightarrow{\text{Iodination}} \underset{\text{Iodal}}{Cl_3CHO} + 3NaOH$$

$$Cl_3CHO + NaOH \xrightarrow{\text{Hydrolysis}} \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod. formate}}{HCOONa}$$

The complete reaction may be written as :

$$CH_3CH_2OH + 4I_2 + 6NaOH \longrightarrow CHI_3 + HCOONa + 5NaI + 5H_2O$$

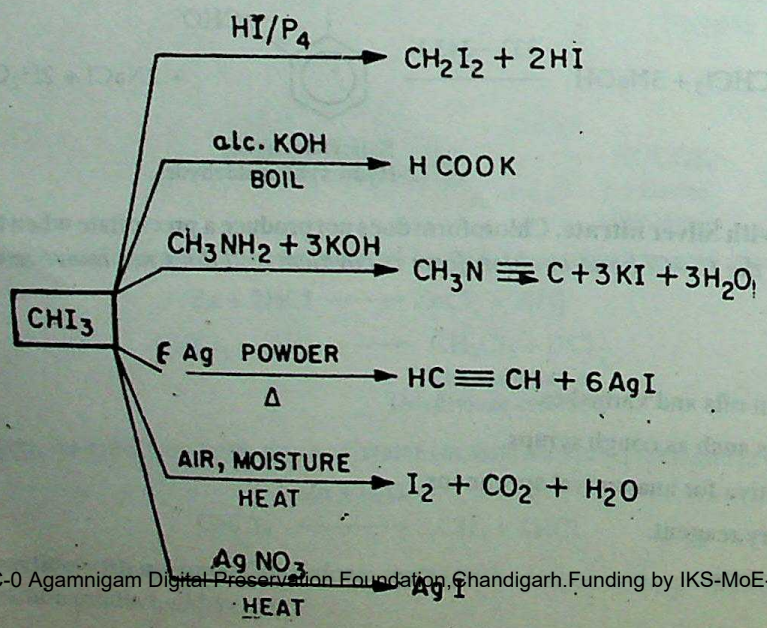
However, when sodium carbonate is used in place of sodium hydroxide then the complete reaction may be written as :

$$CH_3CH_2OH + 4I_2 + 3Na_2CO_3 \longrightarrow CHI_3 + 5NaI + HCOONa + 3CO_2 + 2H_2O$$

Reaction involved in the preparation of CHI_3 *from acetone* are :

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 + 3NaOI \longrightarrow \underset{\text{Triiodoacetone}}{Cl_3-\underset{\underset{O}{\|}}{C}-CH_3} + 3NaOH$$

$$Cl_3-\underset{\underset{O}{\|}}{C}-CH_3 + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sod. acetate}}{CH_3-\underset{\underset{O}{\|}}{C}-ONa}$$



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Physical Properties

Iodoform is a yellow coloured solid having m.p. 382 K. It is insoluble in water but dissolves readily in organic solvents.

Chemical Properties

Chemical reactions of iodoform are similar to that of chloroform and are **summarised** on previous page :

Uses of Iodoform

1. It is used as an antiseptic for dressing wounds
2. It is used to manufacture pharmaceuticals.

Iodoform Test

This test is used for the identification of functional groups like

$CH_3\overset{\overset{O}{\|}}{C}-$ and $CH_3\overset{\overset{OH}{|}}{C}H-$ in organic compounds. *It is observed that when the compounds containing such functional groups are heated with an aqueous solution of Na_2CO_3 or NaOH containing iodine a yellow precipitate of iodoform is obtained.*

Thus, the test helps us to identify such type of groupings in the organic compounds. The reaction involved are :

$$2NaOH + I_2 \longrightarrow NaI + NaOI + H_2O$$

$$CH_3-\underset{\underset{OH}{|}}{\overset{\overset{H}{|}}{C}}-R + NaOI \longrightarrow CH_3-\underset{\underset{O}{\|}}{C}-R + NaI + H_2O$$

$$CH_3-\underset{\underset{O}{\|}}{C}-R + 3NaOI \longrightarrow Cl_3-\underset{\underset{O}{\|}}{C}-R + 3NaOH$$

$$Cl_3-\underset{\underset{O}{\|}}{C}-R + NaOH \longrightarrow \underset{\text{Iodoform}}{CHI_3} + \underset{\text{Sodium salt of acid}}{R-\underset{\underset{O}{\|}}{C}-ONa}$$

Here, R can be H atom or some alkyl group.

Some common pairs which can be distinguished by iodoform test are :

(*i*) ***2-Pentanone and 3-pentanone***

Here, 2-pentanone gives iodoform test positive but 3 pentanone does not.

(*ii*) ***Ethyl alcohol and methyl alcohol***

Ethyl alcohol gives the test positive but methyl alcohol does not.

(*iii*) ***Ethanal and propanal***

Ethanal gives the test positive but propanal does not.

5. Tetrachloromethane (Carbontetrachloride)

Carbon tetrachloride is manufactured by the following methods :

(*i*) **From Methane.** *By chlorination of methane* in the presence of sunlight

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$$CH_4 + 4Cl_2 \xrightarrow{h\nu} CCl_4 + 4\,HCl.$$

(*ii*) **From Carbondisulphide.** By reaction of chlorine with carbondisulphide in the presence of aluminium chloride as catalyst.

$$CS_2 + 3Cl_2 \xrightarrow{AlCl_3} CCl_4 + \underset{\text{Sulphur-monochloride}}{S_2Cl_2}$$

CCl_4 is separated from S_2Cl_2 by fractional distillation.

Physical Properties

Carbon tetrachloride is a colourless, heavy liquid with charactetristic sickly smell. It is heavier than water and is insoluble in water but is soluble in organic solvents such as ether. Carbon tetrachloride is used as solvent for organic reactions.

Chemical Properties

(*i*) **Reduction.** On reduction with moist iron filings, CCl_4 gives chloroform

$$CCl_4 + 2H \xrightarrow{Fe/H_2O} CHCl_3 + HCl$$

(*ii*) **Hydrolysis.** On heating with alc. KOH, it undergoes hydrolysis and gives CO_2 which dissolves in KOH to yield potassium carbonate.

$$CCl_4 + 4KOH \xrightarrow[-4\,KCl]{\Delta} \underset{\text{unstable}}{[C(OH)_4]} \longrightarrow CO_2 + 2H_2O$$

$$2KOH + CO_2 \longrightarrow K_2CO_3 + H_2O$$

(*iii*) **Stability.** CCl_4 is stable to red heat but when the vapours come in contact with water, phosgene is liberated

$$CCl_4 + H_2O \longrightarrow COCl_2 + 2HCl$$

It is because of extra stability to heat that CCl_4 is used as a fire extinguisher under the name pyrene.

(*iv*) **Riemer-Tiemann reaction** (*see Section 7.17*)

(*v*) **Reaction with SbF_3** (*see preparation of freon*)

Uses. 1. As industrial solvent.

2. For the manufacture of chloroform.

3. As laboratory reagent.

4. In dry cleaning.

5. As a fire extinguisher.

6. Dichlorodifluoromethane (Freon), CCl_2F_2

Freon is a non-toxic, non-inflammable, non-corrosive, highly stable, easily liquifiable volatile liquid. It is used as refrigerant and propellant in aerosods. Freon is prepared by the action of antimony fluoride on carbon tetrachloride in the presence of antimony pentachloride.

$$3CCl_4 + 2SbF_3 \xrightarrow{SbCl_5} 2SbCl_3 + \underset{\text{Freon}}{3CCl_2F_2}$$

Since freon has been found to be one of the factors responsible for the depletion of ozone layer, it is being replaced by other harmless compounds in many countries.

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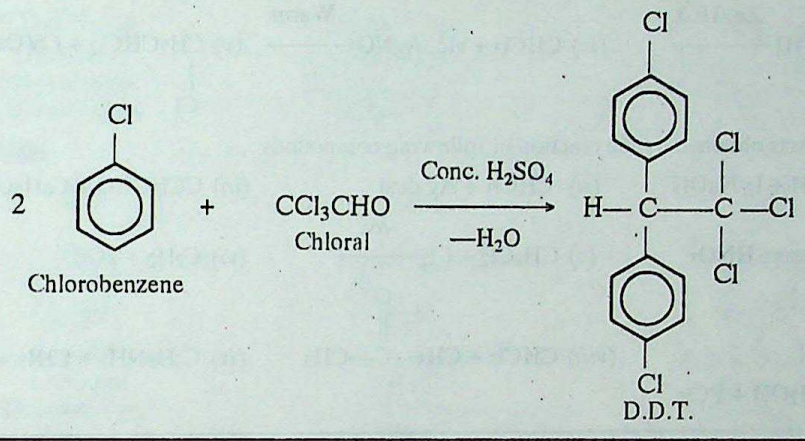
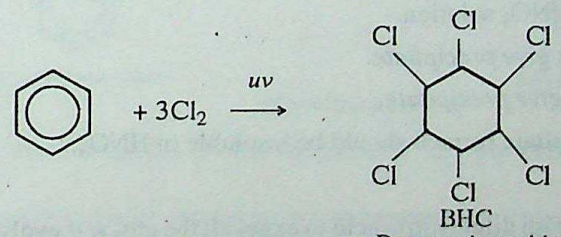
7.1. 1, 1-Trichloro-2, 2-bis (p-chlorophenyl) ethane-(DDT)

DDT is used as an insecticide. It is prepared by heating a mixture of chloral and chlorobenzene in the presence of concentrated sulphuric acid.



Side effects of DDT. DDT is not biodegradable. Its residues accumulate in environment and prove to be toxic to living beings. In human beings it disturbs the sex hormones.

7. **Benzene hexachloride (BHC).** BHC is extensively used as a pesticide in agriculture under the trade name *gammexane* or *Lindane* or *666*. Its IUPAC name is 1, 2, 3, 4, 5, 6-hexachlorocyclohexane. It is manufactured by the chlorination of benzene in the presence of ultraviolet radiation.



8. **Westrosol or Trichloroethylene.** It is prepared by passing 1, 1, 2, 2-tetrachloroethane (Westron) over heated barium chloride, used as a catalyst.

$$\underset{\text{Westron}}{CHCl_2—CHCl_2} \xrightarrow[\Delta]{BaCl_2} \underset{\text{Westrosol}}{CHCl = CCl_2} + HCl$$

Uses. It is used commercially as a solvent for oils, paints, warnishes and particularly in rubber industry.

REVIEW PROBLEMS

7.36. In each of the following pairs of compounds which one gives iodoform test positive.

(*i*) *n*-Propyl alcohol and *iso*-Propyl alcohol (*ii*) *iso*-Butyl alcohol and *sec*-Butyl alcohol

(*iii*) *sec*-Butyl alcohol and *tert*-Butyl alcohol.

7.37. What is the IUPAC name for (*i*) gammexane and (*ii*) westrosol.

7.38. What happens when chloroform is treated with (*i*) Ag powder (*ii*) nitric acid (*iii*) aniline.

7.39. What is the IUPAC name of pyrene and DDT.

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7.40. How will you distinguish between ethyl chloride and vinyl chloride ?

7.41. Complete the following reactions :

(*i*) $CCl_4 + \text{aq. } 4KOH \longrightarrow$ (*ii*) $CHI_3 + CH_3NH_2 + 3KOH \longrightarrow$

(*iii*) $CHCl_3 + 2[H] \xrightarrow{Zn/HCl}$ (*iv*) $CHCl_3 + \text{alc. } AgNO_3 \xrightarrow{Warm}$ (*v*) $CH_2(Cl)CHCl_2 + Ca(OH)_2 \xrightarrow{363\ K}$.

7.42. Name the products obtained by the reaction of following compounds :

(*i*) $CH_3CH_2OH + I_2/NaOH$ (*ii*) $CHCl_3 + \text{Ag dust}$ (*iii*) $CCl_3CHO + C_6H_5Cl$

(*iv*) $CHCl_3 + \text{conc. } HNO_3$ (*v*) $CH_2Cl_2 + Cl_2 \xrightarrow{h\nu}$ (*vi*) $C_2H_2 + 2Cl_2$

(*vii*) $C_6H_6 + 3Cl_2$ (*viii*) $CHCl_3 + CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (*ix*) $C_6H_5NH_2 + CHI_3 + KOH$

(*x*) $CH_2OHCH_2OH + PCl_5$.

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7.9. ANALYSIS OF ALKYL AND ARYL HALIDES

1. Silver nitrate test

In this test, the halide is warmed with aqueous or alcoholic KOH. The solution is then acidified with dil. HNO_3 followed by addition of $AgNO_3$ solution.

Alkyl, benzyl and allyl halides give precipitate.

Aryl and vinyl halides do not give precipitate.

It may be noted that the precipitate formed should be insoluble in HNO_3.

2. Lassaigne's Test

Lassaigne's extract is boiled with dilute nitric acid to expel all the gases, if evolved. Then silver nitrate solution is added to the resulting solution.

If any of the halogen is present, a precipitate is formed :

(*i*) *A white precipitate* soluble in ammonium hydroxide solution indicates the presence of a *chloride.*

(*ii*) *A dull yellow precipitate* partially soluble in ammonium hydroxide solution indicates the presence of a *bromide.*

(*iii*) *A bright yellow precipitate,* completely insoluble in ammonium hydroxide solution, indicates the presence of an *iodide.*

ALCOHOLS AND PHENOLS

Alcohols and phenols are the compounds containing one or more hydroxyl groups (—OH). The alcohols contain the —OH group attached to alkyl group whereas in phenols, the —OH group is attached to aromatic ring. These are classified as *mono-, di-* and *tri hydric* alcohols or phenols according to the number of —OH groups contained in their molecules. Some examples of mono-, di- and trihydric alcohols and phenols are as follows :

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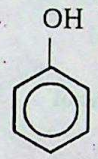
(*a*) **Alcohols**

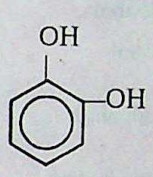
CH_3CH_2OH
Ethanol or
Ethyl alcohol
(*Monohydric*)

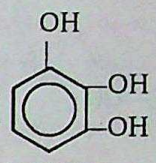
$CH_2(OH)—CH_2(OH)$
1, 2-Ethanediol or
Ethylene glycol
(*Dihydric*)

$CH_2(OH)—CH_2(OH)—CH_2(OH)$
1, 2, 3- Propanentriol or
Glycerol
(*Trihydric*)

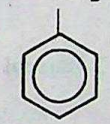
(*b*) **Phenols**

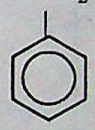

Hydroxybenzene
or Phenol
(*Monohydric*)


1, 2-Dihydroxy-
benzene
or Catechol
(*Dihydric*)


1, 2, 3-Trihydroxy-
benzene
or Pyrogallol
(*Trihydric*)

It may be noted that the *aromatic compounds in which —OH group is not directly attached to benzene ring are not phenols but are called* **aromatic alcohols.** These may be regarded as aryl derivatives of aliphatic alcohols. For example,


Phenyl methanol


2-Phenylethanol

(*Aromatic alcohols*)

When four or more hydroxyl groups are present, they are called *polyhydric alcohols* or *polyhydric phenols.*

Alcohols containing more than one —OH group linked to the same carbon atom are highly unstable and lose water to form more stable aldehydes or ketones.

$$\underset{\text{Unstable}}{CH_3—CH(OH)—OH} \longrightarrow \underset{\text{Ethanal}}{CH_3—CH(H)=O} + H_2O$$

Classification of Alcohols

Monohydric alcohols are classified as primary, secondary or tertiary alcohols depending upon whether the hydroxyl group is attached to a primary, secondary or tertiary carbon atom. For example,

$H_3C—C(H)_2—OH$
Ethyl alcohol
(*Primary*)
or
(1° alcohol)

$H_3C—C(CH_3)(H)—OH$
Isopropyl alcohol
(*Secondary*)
or
(2° alcohol)

$H_3C—C(CH_3)_2—OH$
tert- Butyl alcohol
(*Tertiary*)
or
(3° alcohol)

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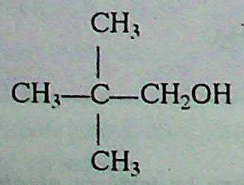
7.10. NOMENCLATURE

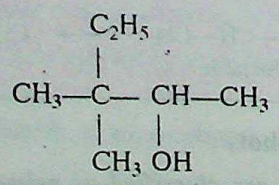
In the common system, alcohols are named as *alkyl alcohols*. In IUPAC system, the names of saturated alcohols are derived from corresponding alkanes by replacing '*e*' of alkanes by '*ol*'. The IUPAC names of a few members of this class are given below :

Formula	*Common Name*	*IUPAC Name*
CH_3OH	Methyl alcohol	Methanol
$CH_3—CH_2—OH$	Ethyl alcohol	Ethanol
$\overset{3}{CH_3}—\overset{2}{CH_2}—\overset{1}{CH_2}—OH$	*n*-Propyl alcohol	1-Propanol
$\overset{3}{CH_3}—\overset{2}{CH}(OH)—\overset{1}{CH_3}$	*iso*-Propyl alcohol	2-Propanol
$\overset{4}{CH_3}—\overset{3}{CH_2}—\overset{2}{CH_2}—\overset{1}{CH_2}—OH$	*n*-Butyl alcohol	1-Butanol
$\overset{3}{CH_3}—\overset{2}{CH}(CH_3)—\overset{1}{CH_2}—OH$	*iso*-Butyl alcohol	2-Methyl-1-propanol
$\overset{1}{CH_3}—\overset{2}{CH}(OH)—\overset{3}{CH_2}—\overset{4}{CH_3}$	*sec*-Butyl alcohol	2-Butanol
$H_3C—\overset{2}{C}(\overset{1}{CH_3})(\overset{3}{CH_3})—OH$	*tert*-Butyl alcohol	2-Methyl-2-propanol

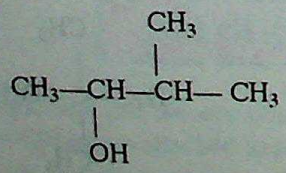
Some more examples of alcohols are given below :



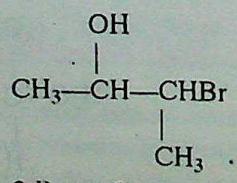
2, 2-Dimethyl-1-propanol



3, 3-Dimethyl-2-pentanol



3-Methyl-2-butanol



3-Bromo-2-butanol

In IUPAC system, dihydric alcohols are named as ***alkanediols*** and trihydric alcohols are named as ***alkanetriols***.

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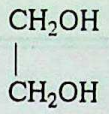
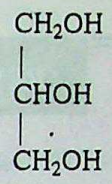
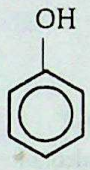


1, 2-Ethanediol
(Ethylene glycol)

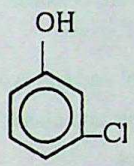


1, 2, 3-Propanetriol
(Glycerol)

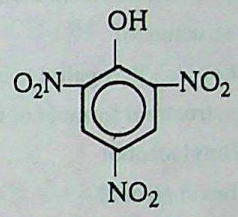
Phenols are named as derivatives of the simplest compound of this class, *i.e.*, phenol.



Phenol

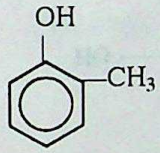


3-Chlorophenol

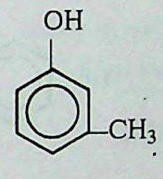


2, 4, 6-Trinitrophenol
(*Picric acid*)

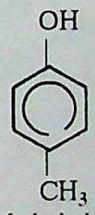
Methyl phenols are known as *cresols*.



2-Methyl phenol
or
o-Cresol

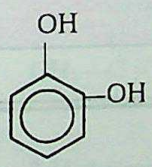


3-Methyl phenol
or
m-Cresol

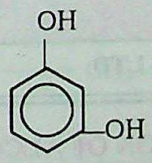


4-Methyl phenol
or
p- Cresol

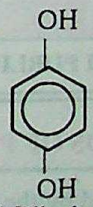
Some dihydric and trihydric phenols are given below :



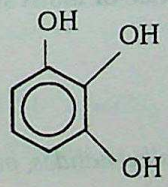
1, 2-Dihydroxy-
benzene
(Catechol)



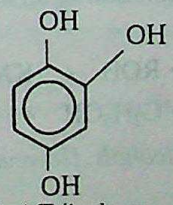
1, 3-Dihydroxy-
benzene
(Resorcinol)



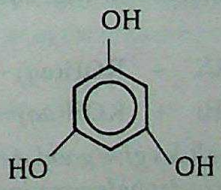
1, 4-Dihydroxy-
benzene
(Quinol)



1, 2, 3-Trihydroxy-
benzene
(Pyrogallol)



1, 2, 4-Trihydroxy-
benzene
(Hydroxyquinol)



1, 3, 5-Trihydroxy-
benzene
(Phloroglucinol)

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REVIEW PROBLEMS

7.43. Give one example of each of the following with its IUPAC name :

(*i*) A secondary monohydric alcohol (*ii*) A dihydric alcohol

(*iii*) A tertiary aromatic alcohol. (*iv*) An optically active aliphatic alcohol.

7.44. How many isomeric alcohol with formula C_4H_9OH are possible.

7.45. Give the structure of

(*i*) Catechol ; (*ii*) Pyrogallol ; (*iii*) *neo*-Pentyl alcohol and (*iv*) *iso*-Amyl alcohol.

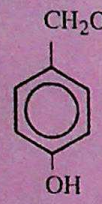
7.46. Write the structural formula of the following alcohols and classify them as 1°, 2° or 3°.

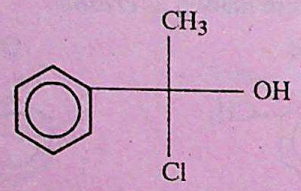
(*i*) sec-Butyl alcohol (*ii*) Allyl alcohol (*iii*) Benzyl alcohol

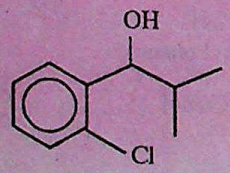
(*iv*) neo-hexyl alcohol (*v*) 2-Methyl-2-butanol.

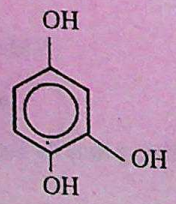
7.47. Give structures of all isomeric alcohols with formula $C_4H_{10}O$. Which amongst these is optically active ?

7.48. Give IUPAC names of the following :

(*i*)


(*ii*)


(*iii*)


(*iv*)


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7.11. GENERAL METHODS OF PREPARATION OF ALCOHOLS

Alcohols are obtained by the following general methods :

(1) By the Hydrolysis of Haloalkanes

Haloalkanes when boiled with aqueous solution of an alkali hydroxide or moist silver oxide furnish alcohols.

$$RX + KOH(aq) \longrightarrow ROH + KX$$

$$C_2H_5Br + KOH(aq) \longrightarrow C_2H_5OH + KBr$$

Primary alkyl halides give good yield of alcohols. However, tertiary alkyl halides, in this reaction give, mainly alkene due to dehydrohalogenation.

$$CH_3-\underset{CH_3}{\overset{CH_3}{C}}-Br + KOH \longrightarrow \underset{\text{Major product}}{CH_3-\overset{CH_3}{C}=CH_2} + KBr + H_2O$$

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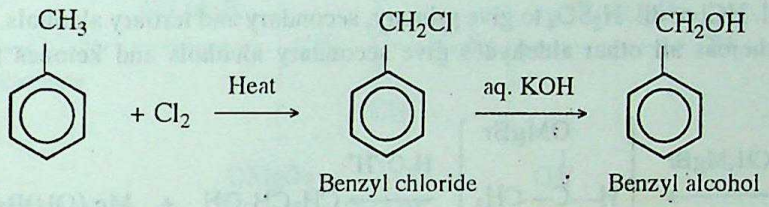
Secondary alkyl halides give a mixture of alcohol and alkene

$$CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow[\text{heat}]{NaOH(aq)} CH_3-\underset{\underset{OH}{|}}{CH}-CH_3 + CH_3CH=CH_2$$

This method is not very useful for preparing alcohols because haloalkanes are themselves obtained from alcohols. However, the preparative utility of this method lies in the praparation of aromatic alcohols. For example,



2. Hydration of Alkenes

The hydration of alkenes can be achieved indirectly by addition of H_2SO_4 to furnish alkyl hydrogen sulphate which on hydrolysis with hot water gives alcohol. For example,

$$\underset{\text{Ethene}}{CH_2=CH_2} + H_2SO_4 \longrightarrow \underset{\text{Ethyl hydrogen sulphate}}{CH_3CH_2HSO_4} \xrightarrow[-H_2SO_4]{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\underset{\text{Propene}}{CH_3-CH=CH_2} + H_2SO_4 \longrightarrow \underset{\text{Iso-Propyl sulphate}}{CH_3\overset{\overset{OSO_3H}{|}}{C}HCH_3} \xrightarrow[-H_2SO_4]{H_2O} \underset{\text{Iso-Propyl alcohol}}{CH_3\overset{\overset{OH}{|}}{C}HCH_3}$$

Some reactive alkenes undergo direct hydration in the presence of mineral acids which act as catalysts.

$$\underset{\text{2-Methylpropene}}{CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2} + H_2O \xrightarrow{H^+} \underset{\text{2-Methyl-2-propanol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{OH}{|}}{C}}-CH_3}$$

Since alkenes are readily obtained by the cracking of petroleum, this method can be used for the manufacture of alcohols.

The indirect addition of water to olefins can also be done through ***hydroboration-oxidation reaction***. In this method alkene is treated with diborane followed by treatment with water in the presence of H_2O_2 when alcohol is formed.

$$\underset{\text{Propene}}{3CH_3CH=CH_2} + \underset{\text{Diborane}}{\tfrac{1}{2}B_2H_6} \longrightarrow \underset{\text{Tripropyl borane}}{(CH_3CH_2CH_2)_3B}$$

$$(CH_3CH_2CH_2)_3B \xrightarrow[OH^-,\ H_2O]{H_2O_2} 3CH_3CH_2CH_2OH + H_3BO_3$$

In this method addition of water occurs in an anti-Markownikoff way.

Alkenes can also be converted to alcohols by ***oxymercuration- demercuration reaction***. In this reaction alkene is treated with mercuric acetate in THF-water solution to yield a product which on reduction with $NaBH_4$ gives alcohol. In this reaction addition occurs according to Markownikoff rule

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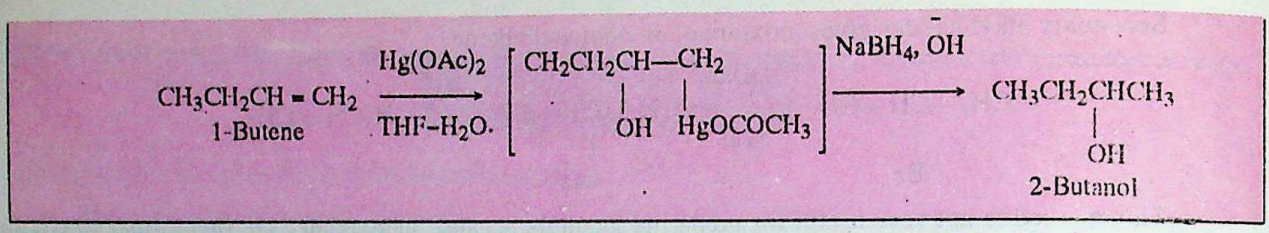
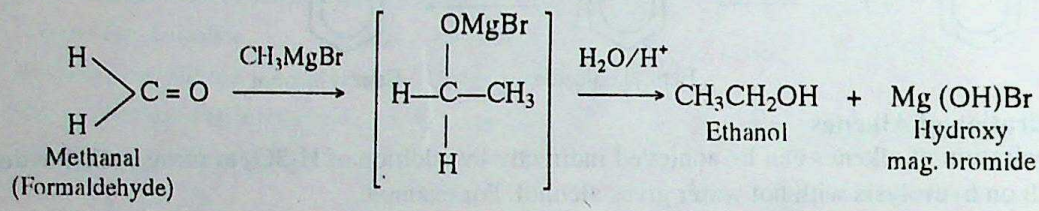
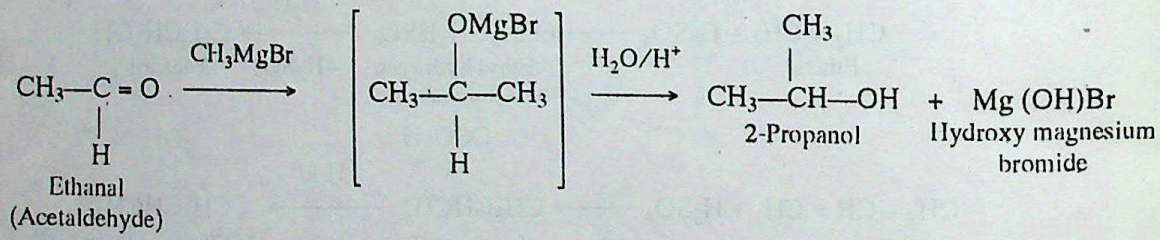
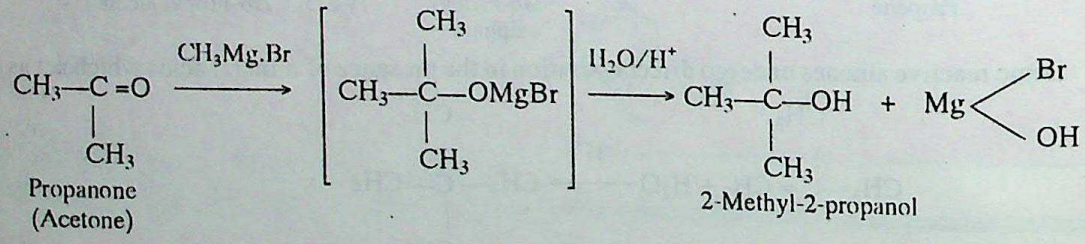


3. From Aldehydes and Ketones

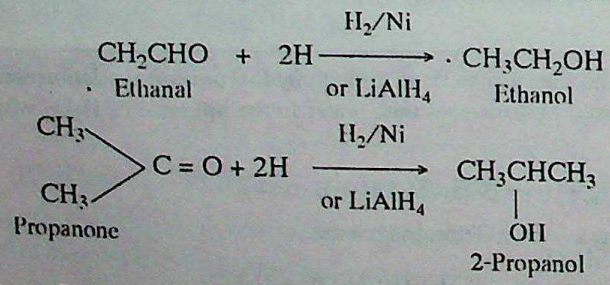
(*a*) *Using Grignard Reagents.* Grignard reagents react with aldehydes and ketones to form products which decompose with dil. HCl or dil. H_2SO_4 to give primary, secondary and tertiary alcohols. Formaldehyde gives primary alcohol whereas all other aldehydes give secondary alcohols and ketones furnish tertiary alcohols.





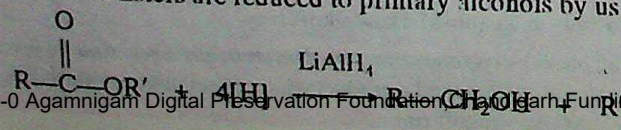


(*b*) *By Reduction.* Aldehydes on reduction give primary alcohols and ketones furnish secondary alcohols. The reducing agents used are *$LiAlH_4$, $NaBH_4$, Na/C_2H_5OH* or *H_2 with Ni, Pt or Pd catalyst.*



4. From Esters

(*a*) *By Reduction.* Esters are reduced to primary alcohols by using $LiAlH_4$ or Na/C_2H_5OH.



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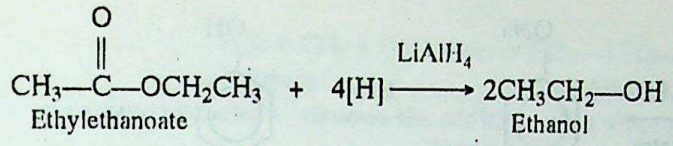
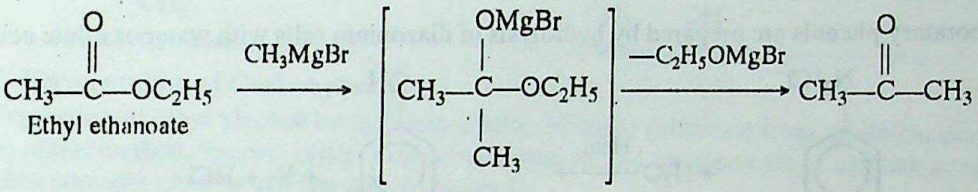
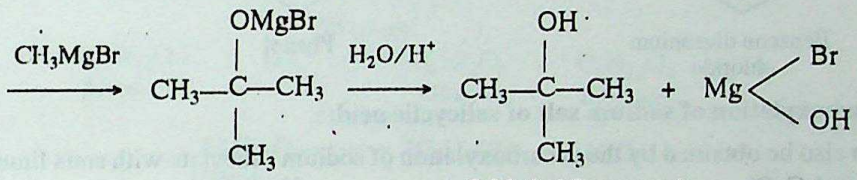
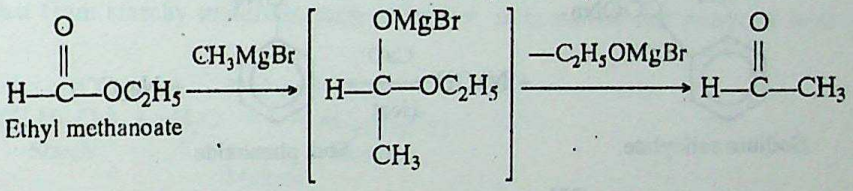


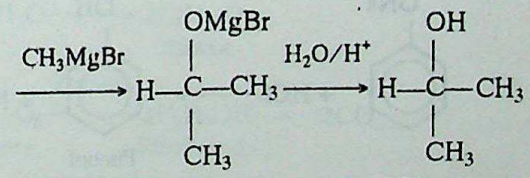
(*b*) *Using Grignard Reagents*. All esters, except that of formic acid, yield tertiary alcohols on reaction with Grignard reagents followed by acidic hydrolysis. Esters of formic acid yield secondary alcohols. For example,





2-Methyl-2-propanol
(*A tertiary alcohol*)





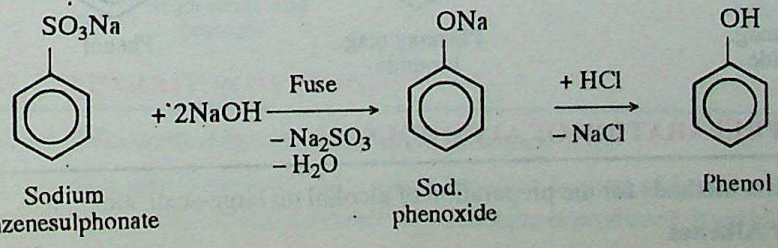
2-Propanol
(*A secondary alcohol*)

7.12. PREPARATION OF PHENOLS

The methods used for the preparation of phenols are given below :

1. Alkali fusion of sulphonates

Sodium salts of sulphonic acids on fusion with NaOH at 573 K followed by acidification yield phenols.



2. From aryl halides (*Dow's process*)

Phenol is obtained on a large scale by heating chlorobenzene with 10% NaOH solution at about 623 K and under a pressure of 300 atmospheres in the presence of copper catalyst.

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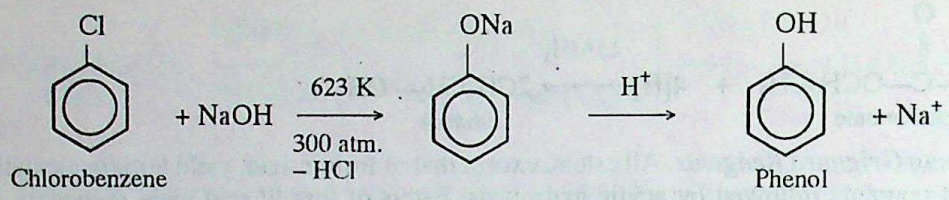
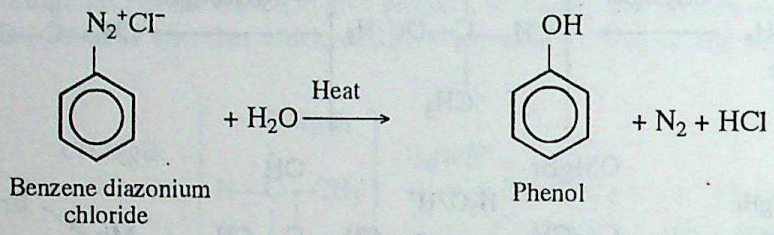


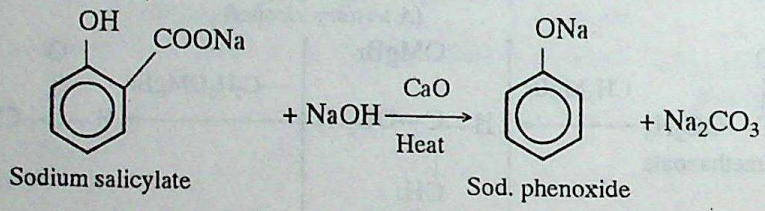
3. From diazonium salts

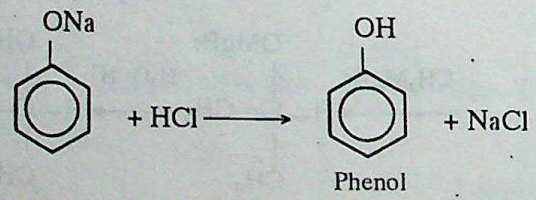
In the laboratory phenols are prepared by hydrolysis of diazonium salts with water or dilute acids.



4. By decarboxylation of sodium salt of salicyclic acid

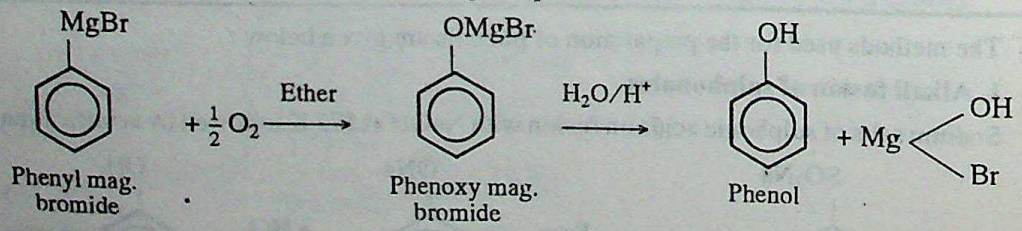
Phenol can also be obtained by the decarboxylation of sodium salicylate with soda lime (an equimolar mixture of NaOH and CaO).





5. From Grignard's reagent

When oxygen is bubbled through the solution of phenylmagnesium bromide in ether, it forms an addition product which on acidification with dilute acid gives phenol.



7.13. INDUSTRIAL PREPARATION OF ALCOHOLS

The two important methods for the preparation of alcohol on large-scale are :

1. Hydration of Alkenes

Alkenes are obtained by cracking of petroleum. They are easily converted to alcohols by the addition of water in presence of sulphuric acid.

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$$\underset{\text{Ethene}}{H_2C = CH_2} + H_2O \xrightarrow{H_2SO_4} \underset{\text{Ethanol}}{CH_3—CH_2—OH}$$

In case of unsymmetrical alkenes, the addition takes place according to Markownikoff's rule.

$$\underset{\text{3-Methyl-1-butene}}{CH_3—\underset{\underset{CH_3}{|}}{CH}—CH = CH_2} + H_2O \xrightarrow{H_2SO_4} \underset{\text{3-Methyl-2-butanol}}{CH_3—\underset{\underset{CH_3}{|}}{CH}—\underset{\underset{OH}{|}}{CH}—CH_3}$$

2. Fermentation of Carbohydrates

Formation of ethyl alcohol by the fermentation of sugar (obtained from mollases, grapes or beet) is one of the oldest method. Sucrose is first converted to glucose and fructose with an enzyme *invertase*. Enzyme *zymase* then converts glucose and fructose to ethanol.

$$\underset{\text{Surcose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{Glucose}}{C_6H_{12}O_6} + \underset{\text{Fructose}}{C_6H_{12}O_6}$$

$$\underset{\text{Glucose or fructose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$

Ethanol is obtained from starchy materials such as barley, rice, maize and potatoes with enzymes *diastase* and *maltase*.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Diastase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

$$\underset{\text{Glucose}}{C_6H_{12}O_6} \xrightarrow{\text{Zymase}} \underset{\text{Ethyl alcohol}}{2C_2H_5OH} + 2CO_2$$

Enzyme diastase is obtained from germinated barley while enzyme maltase and zymase are obtained from yeast.

3. Oxo Process

Alkenes react with carbon monoxide and hydrogen in the presence of $[Co(CO)_4]_2$ as catalyst and at high temperature and pressure to yield aldehydes. Catalytic hydrogenation of aldehydes gives primary alcohols.

$$\underset{\text{Ethene}}{CH_2 = CH_2} + CO + H_2 \xrightarrow[\text{High temp. and pressure}]{[Co(CO)_4]_2} CH_3—CH_2—CHO \xrightarrow{H_2/Ni} \underset{\text{1-Propanol}}{CH_3—CH_2—CH_2—OH}$$

7.14. INDUSTRIAL PREPARATION OF PHENOLS

1. From Cumene. This method has been described in *Section 7.18*.

2. From benzene (Raschig process). The method involves heating of benzene, HCl and air over a catalyst (mixture of $CuCl_2$ and $FeCl_3$) at 500 K when chlorobenzene is produced. It is then heated with super heated steam at 750 K to give phenol.

$$2C_6H_6 + 2HCl + O_2\,(air) \xrightarrow[500\,K]{CuCl_2 + FeCl_2} 2C_6H_5Cl + 2H_2O$$

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$$C_6H_5Cl + H_2O\ (steam) \xrightarrow{750\ K} C_6H_5OH + HCl$$

Another new method for synthesis of phenol is to pass benzene and air over V_2O_5 at 600 K when benzene is directly oxidised to phenol.

$$2C_6H_6 + O_2 \xrightarrow[600\ K]{V_2O_5} 2C_6H_5OH$$

REVIEW PROBLEMS

7.49. Which isomeric alcohols with formula $C_4H_{10}O$ can be prepared by hydrogenation of aldehydes. Give reactions.

7.50. Which alcohol with formula $C_4H_{10}O$ cannot be prepared by the reduction of aldehyde or ketone.

7.51. Name the reagent which is most effective in carrying out anti-Markownikoff's addition of H_2O across ethylenic double bond. Give example.

7.52. What is formed if cyclopentanone is reduced with H_2/Pt ?

7.53. What happens when O_2 is bubbled through phenyl magnesium bromide and the product formed is subjected to hydrolysis ?

7.54. Name the Grignard's reagent required for converting formaldehyde to *n*-butyl alcohol.

7.55. Complete the following equations :

(*i*) $(CH_3)_2C=O \xrightarrow{RMgX} ? \xrightarrow{H^+/H_2O} ?$

(*ii*) $? \xrightarrow[{[CO(CO)_4]}]{[Co + H_2]} ? \xrightarrow{LAH} CH_3—CH_2—CH_2OH$

(*iii*) $C_6H_5Cl \xrightarrow[(CH_3)_2O]{Mg} ? \xrightarrow[(ii)\ H_2O/H^+]{(i)\ O_2\ (air)} ?$

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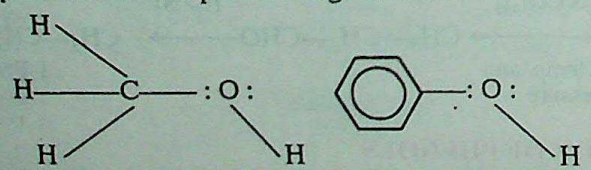
7.15. STRUCTURE OF ALCOHOLS AND PHENOLS

The general formula of alcohols is R—OH, where R is some alkyl or substituted alkyl group. In phenols —OH group is attached to aromatic ring. Since the oxygen atom of the hydroxyl group has two bond pairs and two lone pairs of electrons, therefore, the C— O—H bonds in alcohols as well as phenols is not linear. The structures of the simplest alcohol and phenol are given below :



Methanol Phenol

As oxygen is more electronegative than carbon and hydrogen, therefore, C—O and O—H bonds in alcohols and phenols are polar bonds and hence both alcohols and phenols possess a net dipole moment. Methanol has a dipole moment of 1.71 D whereas phenol has a dipole moment of 1.54 D. *The smaller dipole moment of phenol is due to the electron withdrawing effect of phenyl group in contrast to the electron releasing effect of alkyl group in alcohols.*

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7.16. PHYSICAL PROPERTIES OF ALCOHOLS AND PHENOLS

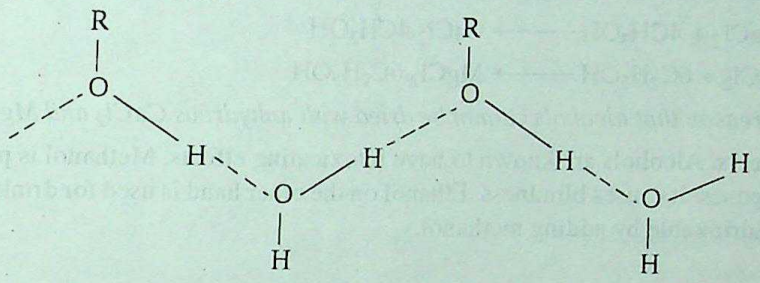
Alcohols

(*i*) The lower members of alcohols are colourless, volatile liquids with a characteristic alcoholic smell and burning taste whereas higher alcohols are odourless and tasteless.

Higher alcohols having 12 or more carbon atoms are colourless waxy solids.

(*ii*) **Solubility of alcohols.** The first three members are completely miscible with water. The solubility rapidly decreases with increase in molecular mass. The higher members are almost insoluble in water but are soluble in organic solvents like benzene, ether, etc.

The solubility of lower alcohols is due to the existence of hydrogen bonds between water and polar O—H group of alcohol molecules.

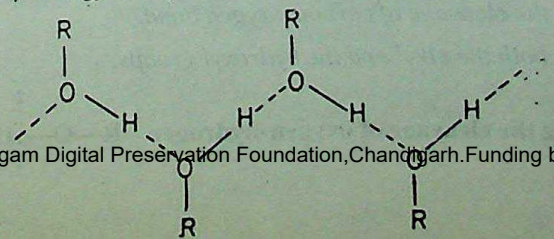


***The solubility of alcohols in water decreases with increase in molecular mass** because with increase in molecular mass, the non-polar alkyl group becomes predominant and masks the effect of polar —OH group.*

In addition, ***among the isomeric alcohols the solubility increases with branching of chain.** It is because the surface area of non-polar part in the molecule decreases, enhancing the solubility.* The argument is well-supported by solubility data of isomeric alcohols, with molecular formula of C_4H_9OH, as listed below.

Alcohol	*Structure*	*Solubility g/100 g of H_2O*
n-Butyl alcohol	$CH_3CH_2CH_2CH_2OH$	7.9
sec-Butyl alcohol	$CH_3CH(OH)CH_2CH_3$	12.5
iso-Butyl alcohol	$(CH_3)_2CH—CH_2OH$	10.0
tert-Butyl alcohol	$CH_3—C(CH_3)_2—OH$	∞

(*iii*) **Boiling points.** Boiling points of alcohols are much higher than those of alkanes, haloalkanes or ethers of comparable molecular masses. *This is because in alcohols intermolecular hydrogen bonding exists due to which a large amount of energy is required to break these bonds.*



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Compound	*Mol. mass*	*Boiling point*
CH_3CH_2OH (Ethanol)	46	351 K
CH_3OCH_3 (Methoxymethane)	46	297 K
CH_3Cl (Chloromethane)	50.5	249 K
$CH_3CH_2CH_3$ (Propane)	44	231 K

For isomeric alcohols the boiling points follow the order :

primary alcohol > secondary alcohol > tertiary alcohol.

(*iv*) Lower alcohols are found to form solid derivatives with $CaCl_2$ and $MgCl_2$

$$CaCl_2 + 4CH_3OH \longrightarrow CaCl_2.4CH_3OH$$

$$MgCl_2 + 6C_2H_5OH \longrightarrow MgCl_2.6C_2H_5OH$$

It is because of this reason that alcohols cannot be dried with anhydrous $CaCl_2$ and $MgCl_2$.

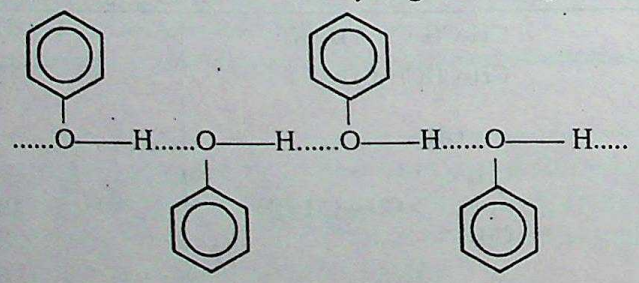
(*v*) **Intoxicating effects.** Alcohols are known to have intoxicating effects. Methanol is poisonous and is not good for drinking purposes. It causes blindness. Ethanol on the other hand is used for drinking purposes. Sometimes it is rendered undrinkable by adding methanol.

Phenols.

(*i*) Phenols are colourless crystalline solid or liquids. However, they become coloured due to slow oxidation with air.

(*ii*) Phenols have characteristic odours and are sparingly soluble in water but readily soluble in organic solvents such as alcohol and ether.

(*iii*) Phenols boil at higher temperatures than the arenes of comparable molecular masses. For example, b.p. of phenol (molecular mass = 94) is 453 K while that of toluene (molecular mass = 92) is 384 K. The higher b.p. of phenols is due to the presence of intermolecular hydrogen bonding in them.



7.17. CHEMICAL PROPERTIES OF ALCOHOLS

In alcohols, —OH group is the functional group. Therefore, the chemical properties of alcohols generally involve the reactions of —OH group. These can undergo **substitution** as well as **elimination** reaction. The chemical reactivity of alcohols depends upon the carbon chain attached to —OH group. The reactions of alcohols can be classified into three types :

1. *Reactions involving the cleavage of oxygen-hydrogen bond.*
2. *Reactions involving the cleavage of carbon-oxygen bond.*
3. *Reactions involving both the alkyl and the hydroxyl groups.*

1. Reactions involving the cleavage of oxygen-hydrogen $\left(R—O—\overset{\vdots}{\underset{\vdots}{H}}\right)$ **bond.**

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(*a*) **Acidic character.** Alcohols are very weak acids (Ka = $10^{-16} - 10^{-18}$) even feeble than water (Ka = 10^{-14}). They do not turn blue litmus red but when treated with active metals like sodium or potassium these liberate hydrogen along with the formation of alkoxides.

$$R—O—H + Na \longrightarrow R—\overset{-}{O}\overset{+}{Na} + \frac{1}{2}H_2$$

Sod. alkoxide

$$C_2H_5OH + Na \longrightarrow C_2H_5—\overset{-}{O}\overset{+}{Na} + \frac{1}{2}H_2$$

Ethanol Sod. ethoxide

Alcohols behave as acids because of the presence of polar O—H group. Due to greater electronegativity of oxygen atom the shared pair between O and H is drawn towards the oxygen atom helping in release of H^+ ion. However, the release of H^+ ion in alcohols does not take place with ease and hence the alcohols act as very weak acids. This is explainable on the basis of electron releasing nature of alkyl group present in alcohols. This electron releasing tendency of alkyl group increases electron density around the oxygen atom due to which

$$\mathbf{R \rightarrow \ddot{\underset{..}{O}} - H \rightleftharpoons R \rightarrow \ddot{\underset{..}{O}}^- : + H^+}$$

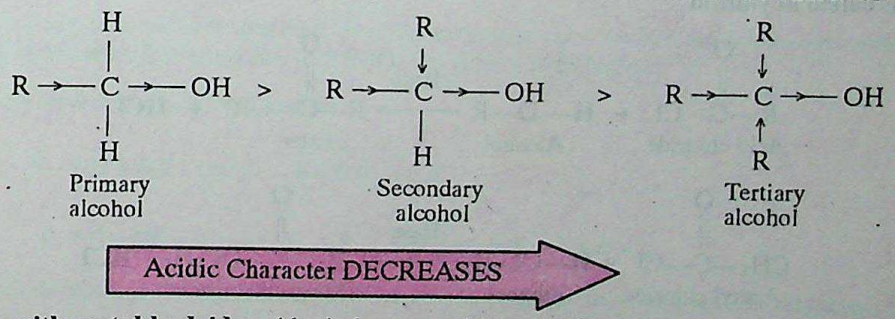
Alcohol **Alkoxide ion.**

the polarity of the O—H bond decreases. In addition the alkoxide ion formed is also destablized due to concentration of negative charge on oxygen atom by electron releasing inductive effect of alkyl group. Thus, the release of H^+ ion is difficult. This explains the weak acidic character of alcohols.

The order of ***acidic strength*** among various types of alcohols is

primary > secondary > tertiary

The order can also be explained in terms of electron releasing inductive effect of alkyl groups. Greater is the number of alkyl groups attached to the carbon carrying the —OH group lesser shall be the polarity of OH group and hence lesser will be the acidic character. In tertiary alcohols, the carbon atom, carrying —OH is attached to three alkyl groups, due to which electron density on oxygen is maximum in their case and hence the loss of H^+ is most difficult. Thus, tertiary alcohols are least acidic, whereas primary alcohols (with only one alkyl group) are most acidic. However, secondary alcohols have intermediate acidic character.



(*b*) **Reaction with metal hydrides.** Alcohols react with metal hydrides to form salts alongwith th evolution of hydrogen gas.

$$ROH + NaH \longrightarrow R\overset{-}{O}\overset{+}{Na} + H_2$$

$$CH_3OH + NaH \longrightarrow CH_3\overset{-}{O}\overset{+}{Na} + H_2$$

Methanol Sod. methoxide

(*c*) **Reaction with Grignard's reagent.** Alcohols react with Grignard's reagent to form alkanes. In *these reactions, the alkane is obtained from the alkyl part of Grignard's reagent.*

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$$R{-}O{-}H + R'{-}Mg{-}X \longrightarrow R'{-}H + Mg\begin{cases} X \\ OR \end{cases}$$

Alcohol, Grignard reagent, Alkane, Alkoxy magnesium halide

$$C_2H_5{-}OH + CH_3{-}Mg{-}Br \longrightarrow CH_4 + Mg\begin{cases} Br \\ OC_2H_5 \end{cases}$$

Methyl magnesium bromide, Methane

This reaction is used for the estimation of alcohlic group (**Zerewitnoff reaction**).

(*d*) **Reaction with monocarboxylic acids** (*Esterification*). Alcohols react with monocarboxylic acids in the presence of conc. sulphuric acid to form esters. The function of conc. H_2SO_4 is to act as a protonating agent as well as a dehydrating agent. The reaction is called **esterification.**

$$\underset{\text{Acid}}{R{-}\overset{\overset{O}{\|}}{C}{-}OH} + \underset{\text{Alcohol}}{H{-}OR'} \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{Ester}}{R{-}\overset{\overset{O}{\|}}{C}{-}OR'} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OH} + \underset{\text{Ethanol}}{H{-}OC_2H_5} \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OC_2H_5} + H_2O$$

This reaction is reversible in nature and the equilibrium can be shifted to the right by removing water as soon as it is formed.

(*e*) **Reaction with acid chloride or acid anhydride** (*Acylation*). When treated with acid chloride or acid anhydride in the presence of bases like pyridine or dimethylaniline (as catalyst) alcohols form esters. This reaction is called **acylation.**

$$\underset{\text{Acid chloride}}{R{-}\overset{\overset{O}{\|}}{C}{-}Cl} + \underset{\text{Alcohol}}{H{-}O{-}R'} \xrightarrow{\text{Base}} \underset{\text{Ester}}{R{-}\overset{\overset{O}{\|}}{C}{-}OR'} + HCl$$

$$\underset{\text{Acetyl chloride}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}Cl} + \underset{\text{Ethanol}}{H{-}OC_2H_5} \xrightarrow{\text{Base}} \underset{\text{Ethyl ethanoate}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}OC_2H_5} + HCl$$

$$\underset{\text{Acid anhydride}}{R{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}R} + \underset{\text{Alcohol}}{H{-}OR'} \longrightarrow \underset{\text{Ester}}{R{-}\overset{\overset{O}{\|}}{C}{-}OR'} + \underset{\text{Acid}}{R{-}\overset{\overset{O}{\|}}{C}{-}OH}$$

$$\underset{\text{Acetic anhydride}}{CH_3{-}\overset{\overset{O}{\|}}{C}{-}O{-}\overset{\overset{O}{\|}}{C}{-}CH_3} + \underset{\text{Ethanol}}{H{-}O{-}C_2H_5} \longrightarrow \underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + \underset{\text{Ethanoic acid}}{CH_3COOH}$$

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2. Reactions involving cleavage of carbon-oxygen $\left(R-\overset{|}{\underset{|}{C}} \vdots -OH \right)$ **bond.**

(a) Reaction with hydrogen halides. As already discussed in *Section 7.2*, hydrogen halides react with alcohols to form alkyl halides. The various reactions are summarized below :

$$R-OH \xrightarrow{HCl/Zn} R-Cl + H_2O$$

$$R-OH \xrightarrow[\text{or } NaBr + \text{Conc. } H_2SO_4]{48\% \ HBr} R-Br + H_2O$$

$$R-OH \xrightarrow[\text{or } KI + H_3PO_4]{57\% \ HI} R-I + H_2O$$

The order of reactivity of various alcohols towards this reaction is

tertiary > secondary > primary

The order of reactivity of various hydrogen halides is in the order

HI > HBr + HCl

Mechanism

For secondary and tertiary alcohols a S_N^1 ***mechanism*** is proposed

1. $$R-OH + HX \rightleftharpoons R-\overset{+}{O}H_2 + :\overset{-}{X}$$

2. $$R-\overset{+}{O}H_2 \rightleftharpoons R^+ + H_2O$$

3. $$R^+ + :X^- \longrightarrow R-X$$

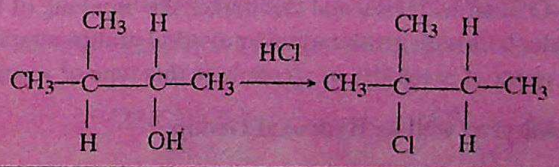
In the step 1, the alcohol accepts hydrogen ion to form the protonated alcohol which dissociates into ***carbocation*** and water in step 2, the carbocation than combines with halide ion is form alkyl halide.

Primary alcohols react through S_N^2 ***mechanism***

1. $$R-OH + HX \rightleftharpoons R-\overset{+}{O}H_2 + :X^-$$

2. $$:X^- + R-\overset{+}{O}H_2 \longrightarrow [\overset{\delta-}{X}.....R.....\overset{\delta+}{O}H_2] \longrightarrow X-R + H_2O$$

In case of alcohols reacting through S_N^1 mechanism the alkyl group may undergo rearrangement due to rearrangement in the intermediate carbocation



(*b*) Reactions with Phosphorous Halides

(*i*) *With* PCl_5. Alcohols react with PCl_5 to from chloroalkanes.

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$$\underset{\text{Alcohol}}{ROH} + \underset{\text{Phosphorus pentachloride}}{PCl_5} \longrightarrow \underset{\text{Alkyl chloride}}{RCl} + \underset{\text{Phosphorus oxy chloride}}{POCl_3} + HCl\uparrow$$

$$\underset{\text{Ethanol}}{C_2H_5OH} + PCl_5 \longrightarrow \underset{\text{Chloroethane}}{C_2H_5Cl} + POCl_3 + HCl\uparrow$$

(*ii*) *With phosphorus trihalides*. Alcohols react with phosphorus trihalides (PCl_3, PBr_3 or PI_3) to form alkyl halides.

$$3ROH + PX_3 \longrightarrow 3RX + H_3PO_3$$

$$3C_2H_5OH + PCl_3 \longrightarrow 3C_2H_5Cl + \underset{\text{Phosphorus acid}}{H_3PO_3}$$

PBr_3 and PI_3 are generally prepared in *situ* by the reaction between phosphorus and bromine or iodine.

$$\underset{\text{Ethanol}}{3C_2H_5OH} + PI_3 \xrightarrow{(P_4 + I_2)} \underset{\text{Iodoethane}}{2C_2H_5I} + H_3PO_3$$

(*c*) **Reaction with thionyl chloride ($SOCl_2$).** Alcohols react with $SOCl_2$ in the presence of pyridine to form chloroalkanes.

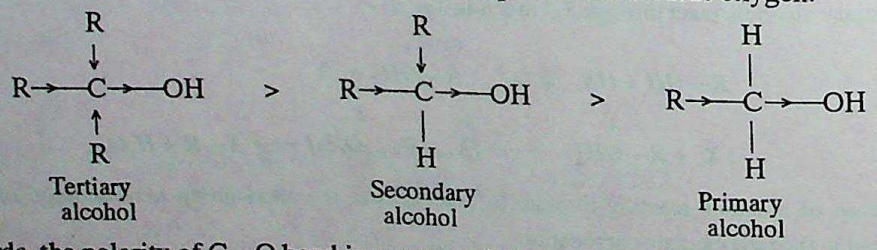
$$\underset{\text{Alcohol}}{ROH} + \underset{\text{Thionyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} \underset{\text{Alkyl chloride}}{RCl} + SO_2\uparrow + HCl\uparrow$$

$$\underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Thionoyl chloride}}{SOCl_2} \xrightarrow{\text{Pyridine}} C_2H_5Cl + SO_2\uparrow + HCl\uparrow$$

The **order of reactivity** of various alcohols towards this type of reactions is

tertiary > secondary > primary.

This can be explained in terms of electron releasing inductive effect of alkyl groups. The alkyl groups by their electron releasing effect tend to increase the electron displacement towards oxygen.



In other words, the polarity of C—O bond increases and this makes the breaking of the bond between carbon and oxygen easier. Therefore, the alcohols with greater number of alkyl groups attached to carbon will be more reactive. This justifies the above order of reactivity of alcohols in this type of reactions.

3. Reactions involving both the Alkyl as well as Hydroxyl Group

The important reactions of this type are :

(*a*) *Acidic dehydration (Reaction with conc. H_2SO_4)*

(*b*) *Oxidation*

(*c*) *Dehydrogenation.*

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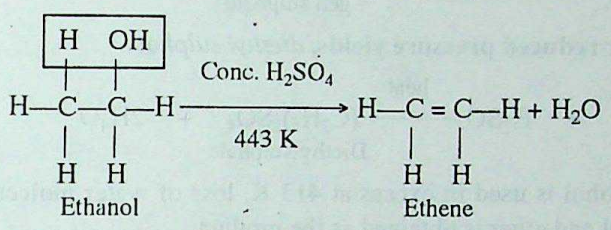
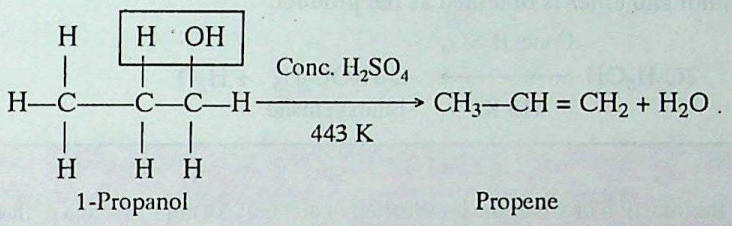
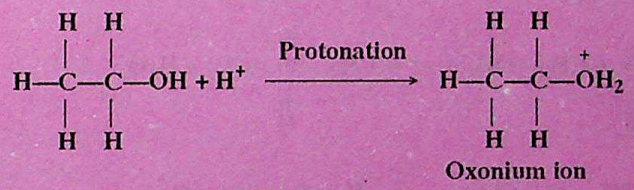
(*a*) **Acidic dehydration** (*Formation of alkenes*). When heated with conc. H_2SO_4, phosphoric acid or boric acid alcohols undergo dehydration to form alkenes. The reaction with conc. sulphuric acid is carried at 443 K, whereas phosphoric acid and boric acid react at higher temperature.

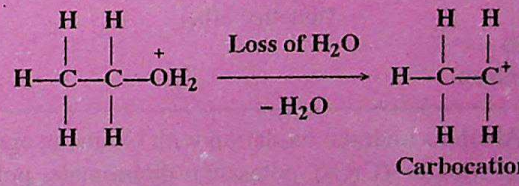


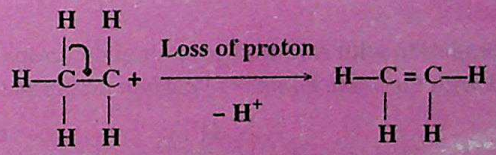


Mechanism of Dehydration of Alcohols

The **mechanism** of this reaction involves protonation of the alcohol followed by loss of a water molecule and a proton.

1. 

2. 

3. 

The ease of dehydration of alcohols follows the order

tertiary alcohol > secondary alcohol > primary alcohol.

Alcohols can also be dehydrated by passing vapours of alcohol over alumina at 620 K.

$$\underset{\text{Ethanol}}{CH_3CH_2OH(g)} \xrightarrow[-H_2O]{Al_2O_3,\ 620\ K} \underset{\text{Ethene}}{CH_2 = CH_2}$$

The reaction between ethanol and sulphuric acid produces different products under different reaction conditions :

(*i*) **At 383 K,** *ethyl hydrogen sulphate* is obtained.

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$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + H_2SO_4 \xrightarrow{383\ K} \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5HSO_4} + H_2O$$

(*ii*) **Distillation under reduced pressure yields,** *diethyl sulphate.*

$$2C_2H_5OH + H_2SO_4 \xrightarrow{heat} \underset{\text{Diethylsulphate}}{(C_2H_5)_2SO_4} + 2H_4O$$

(*iii*) **At 413 K.** If alcohol is used in excess at 413 K, loss of water molecule takes place from two different molecules of alcohol and *ether* is obtained as the product.

$$2C_2H_5OH \xrightarrow[413\ K]{Conc.\ H_2SO_4} \underset{\text{Ethoxyethane}}{C_2H_5OC_2H_5} + H_2O$$

Mechanism

The *mechanism* of this reaction involves the protonation of alcohol. An unprotonated molecule of alcohol then combines with the protonated molecule of alcohol with a loss of water molecule. The oxonium ion formed gives ether by loss of a proton as given below :

1. $$CH_3—OH + H^+ \longrightarrow CH_3—\overset{\oplus}{O}H_2$$

2. $$CH_3—\ddot{O}: + CH_3—\overset{+}{O}H_2 \longrightarrow CH_3—\overset{\oplus}{O}—CH_3 + H_2O$$
(H bonded to the O of $CH_3—\ddot{O}:$; H bonded to the O of $CH_3—\overset{\oplus}{O}H_2$)

3. $$CH_3—\overset{+}{O}—CH_3 \longrightarrow \underset{\text{Dimethyl ether}}{CH_3—O—CH_3} + H^+$$
(H bonded to the O of $CH_3—\overset{+}{O}—CH_3$)
Oxonium ion

(*b*) **Oxidation of alcohols.** Alcohols undergo oxidation with oxidising agents (in neutral or acidic or alkaline medium) such as chromium trioxide (CrO_3), potassium dichromate, potassium permanganate and nitric acid.

(*i*) ***A primary alcohol*** on oxidation with acidified potassium dichromate first gives an aldehyde which on further oxidation gives an acid with the *same number of carbon atoms* as the original alcohol.

$$\underset{\text{Primary alcohol}}{R—CH_2—OH} + [O] \xrightarrow[-H_2O]{K_2Cr_2O_7/H^+} \underset{\text{Aldehyde}}{R—CH=O} \xrightarrow{+[O]} \underset{\text{Acid}}{R—C(OH)=O}$$

$$\underset{\text{Ethanol}}{CH_3—CH_2—OH} + [O] \xrightarrow[-H_2O]{K_2Cr_2O_7/H^+} \underset{\text{Ethanal}}{CH_3—CH=O} \xrightarrow{+[O]} \underset{\text{Ethanoic acid}}{CH_3—C(OH)=O}$$

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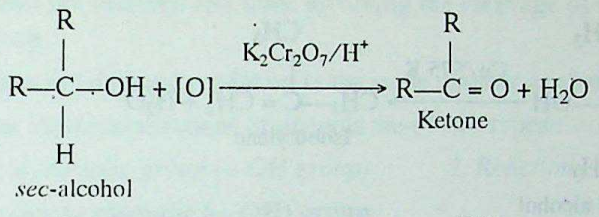
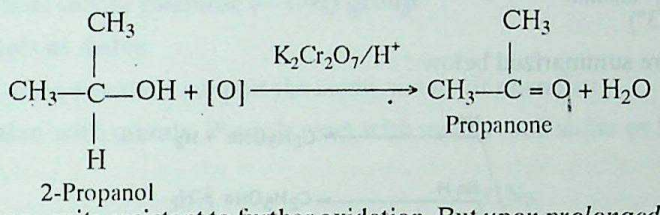
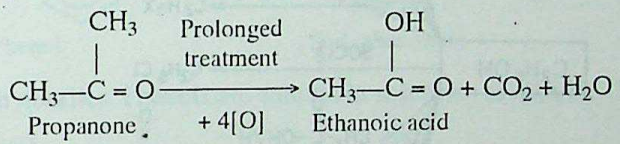
(*ii*) ***A secondary alcohol*** on oxidation first gives a ketone with the same number of carbon atoms as the original alcohol.

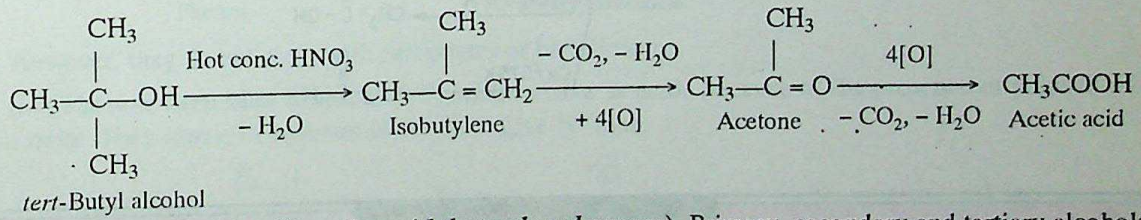




Ketones are quite resistant to further oxidation. But *upon prolonged treatment with the oxidising agent they get oxidised to acids with lesser number of carbon atoms than the alcohol.* The reaction is **oxidative degradation** of alcohols.

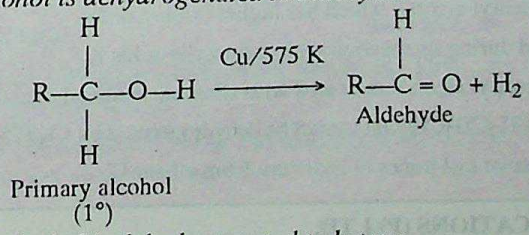


(*iii*) ***Tertiary alcohols*** are not oxidised with mild oxidising agents in aqueous, alkaline or under neutral conditions. However, when oxidation is carried out under acidic conditions, tertiary alcohols first undergo dehydration to form alkene. The alkene formed is then oxidized to ketone which is finally oxidised to carboxylic acid with lesser number of carbon atoms than the starting alcohol.

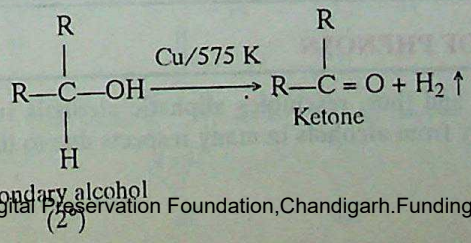


(*c*) **Dehydrogenation** (***Reaction with hot reduced copper***). Primary, secondary and tertiary alcohols give different products when their vapours are passed through a tube packed with reduced copper at 575 K.

(*i*) *A primary alcohol is dehydrogenated to aldehyde.*



(*ii*) *A secondary alcohol is dehydrogenated to ketone*



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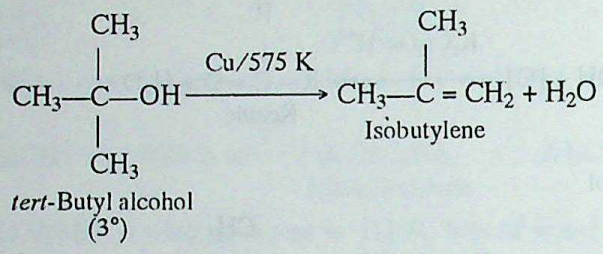
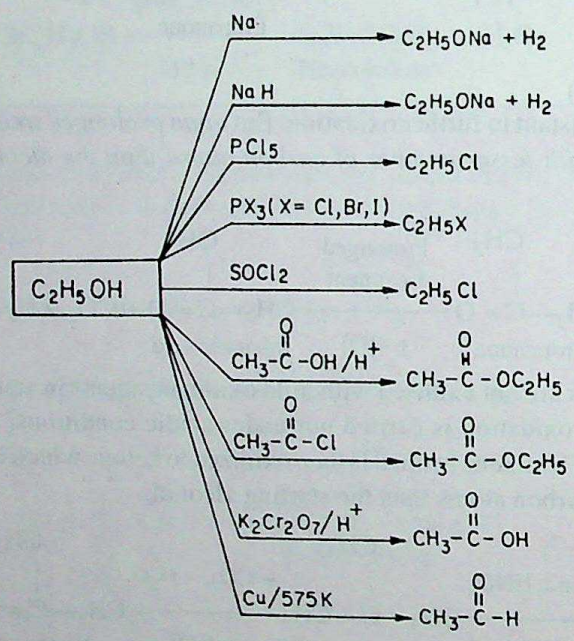
(*iii*) *Tertiary alcohol* does not dehydrogenate due to absence of α-hydrogen. However, it *gets dehydrated to from an alkene.*



The reactions of alcohols are summarized below :



REVIEW PROBLEMS

7.56. Out of neopentyl alcohol and *n*-pentyl alcohol which has higher boiling point.

7.57. Which bond of alcohol is cleaved during its reaction with carboxylic acids ?

7.58. Which ester is formed when isopropyl alcohol is treated with ethanoic acid and conc. H_2SO_4 ? Give reaction.

7.59. Which structural isomer of $CH_3CH_2CH_2CH_2OH$ cannot be dehydrogenated by Cu/575 K.

7.60. Can sodium metal be used to remove last traces of moisture from ethanol ?

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7. 18. CHEMICAL PROPERTIES OF PHENOLS

Phenol contains —OH group and thus, resembles aliphatic alcohols in may respects. Apart from similarities, phenol behaves differently from alcohols in many respects due to the presence of benzene ring. For example :

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(*i*) Phenol does not undergo elimination reaction to form olefins.

(*ii*) Phenol does not undergo reactions involving the cleavage of C—OH bond or substitution of the —OH group.

(*iii*) Phenol does not undergo oxidation in the same manner as alcohols but forms complex products.

In general, the chemical reactions of phenols are of two types :

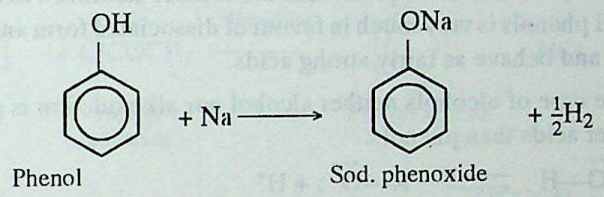
1. *Reactions of phenolic group (—OH group)* 2. *Reactions of benzene ring.*

1. Reactions due to phenolic (—OH) group

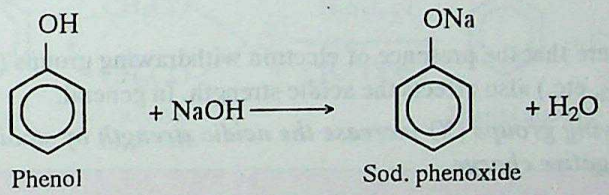
(*a*) **Phenols as Acids**

The following reactions support the acidic nature of phenols :

(*i*) **Reaction with metals.** Phenols react with metals such as Na or K to form salt and hydrogen gas is liberated.

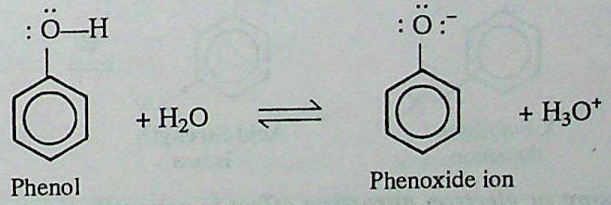


(*ii*) **Reaction with alkalies.** Phenols are soluble in solutions of alkalies (NaOH or KOH).



However, they do not react with carbonates or bicarbonates.

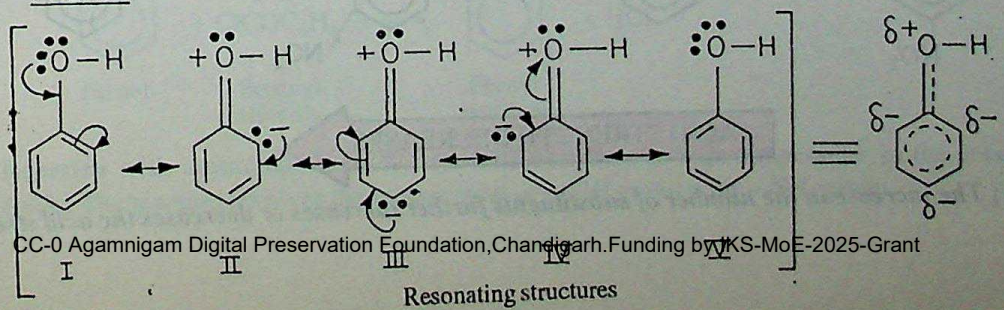
(*iii*) **Phenols turn blue litmus red.** Phenols behave as acids because of the presence of polar O—H group in them. They ionise in aqueous solutions to give H^+ ions.



Phenols behave as stronger acids than alcohols. This can be explained by considering relative stabilities of phenol and phenoxide ion.

Phenol as well as phenoxide ion both are resonance stabilized. The various contributing structures of phenol and phenoxide ion are given below :

PHENOL



Resonating structures

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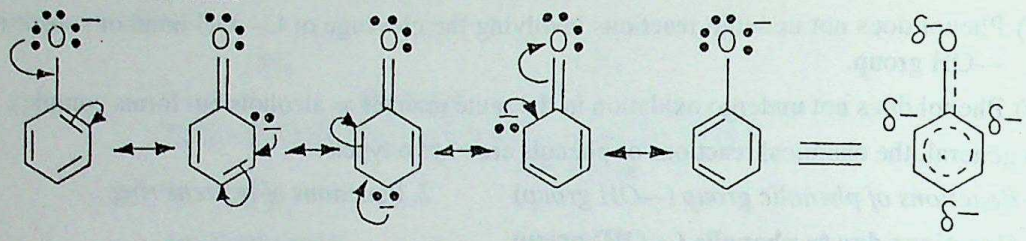
PHENOXIDE ION



Resonating structures

If we observe these structures, then we find that phenoxide ion is more stabilized by resonance than phenol. In phenol, three contributing structures (II, III and IV) involve charge separation whereas in case of phenoxide ion there is no charge separation. Since phenoxide ion is more stabilized than phenol, therefore, the equilibrium in the dissociation of phenols is very much in favour of dissociated form and hence phenols furnish a high concentration of H^+ ions and behave as fairly strong acids.

On the other hand, in the case of alcohols neither alcohol nor alkoxide ion is stabilized by resonance and hence they behave as weaker acids than phenols.

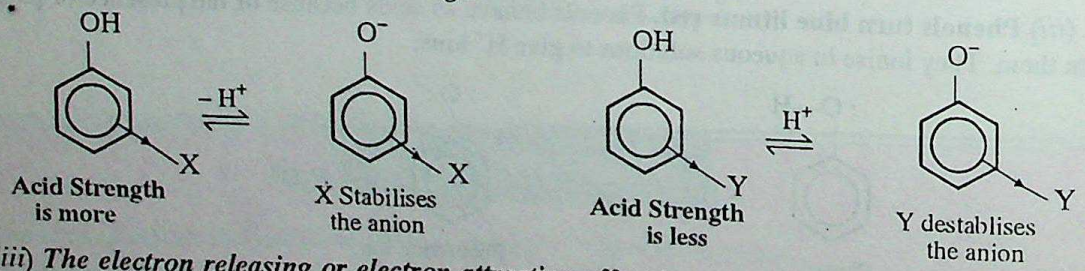
$$R-\ddot{\underset{..}{O}}-H \rightleftharpoons R-\ddot{\underset{..}{O}}^{-} : + H^+$$

The above arguments are also supported by the value of dissociation constants of phenol ($Ka = 10^{-10}$) and alcohol ($Ka = 10^{16}—10^{18}$)

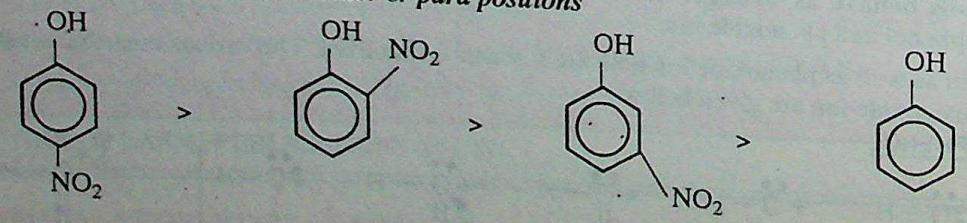
It must be further noted here that the presence of electron withdrawing groups (NO_2, CHO, etc.) and electron releasing groups (R, NH_2, etc.) also affects the acidic strength. In general,

(*i*) ***the electron withdrawing groups (X) increase the acidic strength by stabilizing the phenoxide ion by dispersal of negative charge.***

(*ii*) ***the electron releasing groups (Y) decrease the acidic strength by destabilizing the phenoxide ion by concentrating the negative charge.***



(*iii*) ***The electron releasing or electron attracting effect is generally more pronounced if the substituent is present at the another or para positions***



ACID STRENGTH DECREASES

(*iv*) ***The increase in the number of substituents further increases or decreases the acid strength.***

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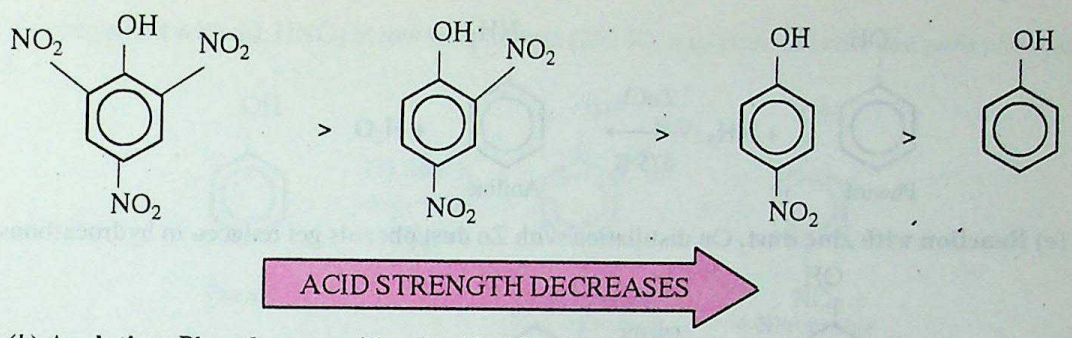
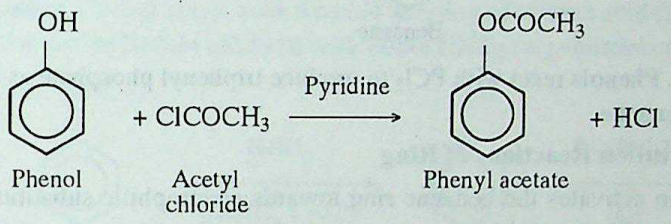
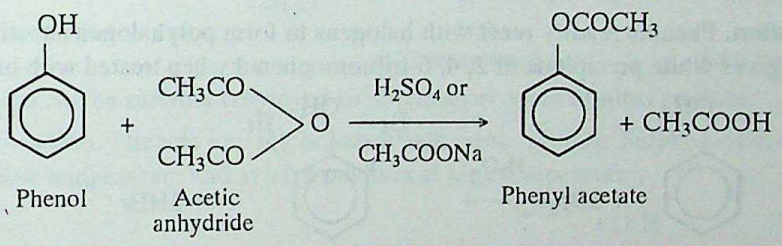
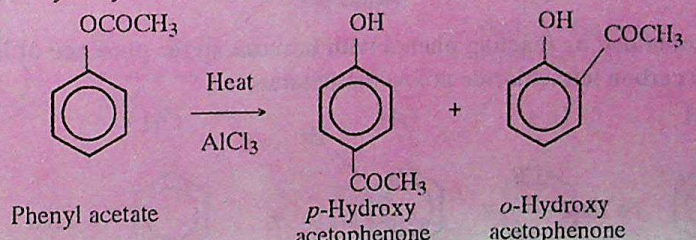


(*b*) **Acylation.** Phenols react with acid chlorides (in the presence of pyridine) or with acid anhydrides (in the presence mineral acids like H_2SO_4 or base pyridine or sod. acetate) to form esters.

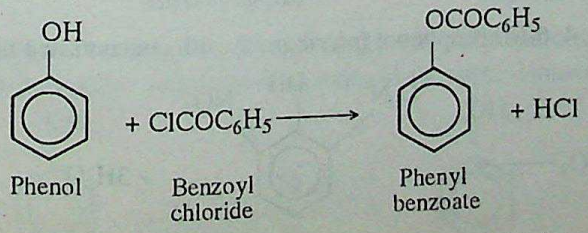




Phenyl esters on heating with anhydrous $AlCl_3$ in the presence of CS_2 as solvent undergo rearrangement to give ortho and para hydroxy ketones. This rearrangement is known as **Fries Rearrangement.**



(*c*) **Benzoylation.** Phenols react with bonzoyl chloride in the presence of aqueous NaOH to from phenyl benzoate. The reaction is known as **Schotten Baumann** reaction.



(*d*) **Reaction with ammonia.** Phenols react with ammonia at high temperature in the presence of anhydrous $ZnCl_2$. The reaction involves the replacement of —*OH* group with —NH_2 group.

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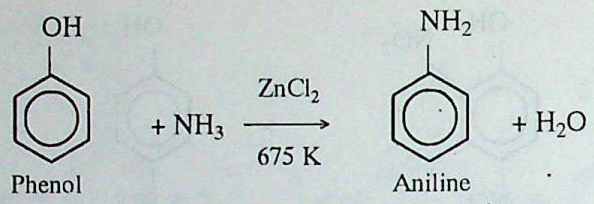
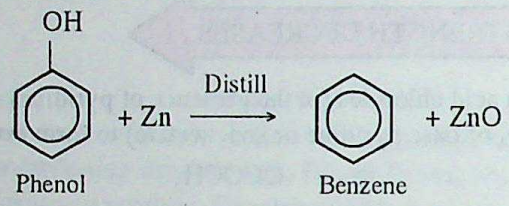


(*e*) **Reaction with zinc dust.** On distillation with Zn dust phenols get reduced to hydrocarbons.

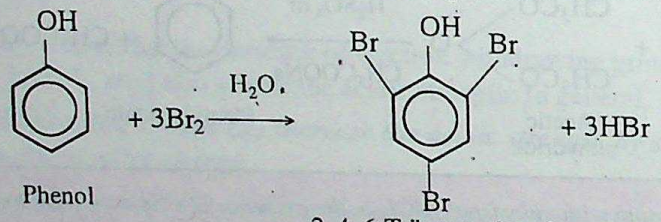


(*f*) **Reaction with PCl_5.** Phenols react with PCl_5 to produce triphenyl phosphate as the major product and a small amount of chlorobenzene.

2. Electrophilic Substitution Reactions of Ring

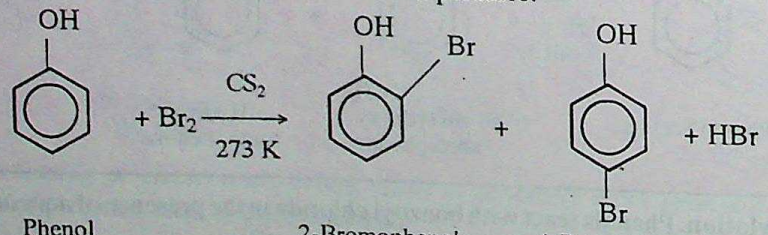
In phenols, —OH group activates the benzene ring towards electrophilic substitution reactions and directs the substitution at *ortho* and *para* positions.

(*a*) **Halogenation.** Phenols readily react with halogens to form polyhalogen substituted compounds. For example, phenol gives white precipitate of 2, 4, 6-tribromophenol when treated with bromine water.



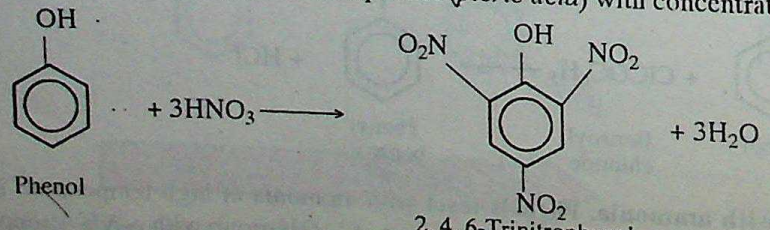
2, 4, 6-Tribromophenol
(white ppt.)

Monobromophenol is obtained by reacting phenol with bromine in the presence of less polar solvent such as a carbon disulphide or carbon tetrachloride at low temperature.



(*Major product*)

(*b*) **Nitration.** Phenol forms 2, 4, 6-trinitrophenol (*picric acid*) with concentrated nitric acid.



2, 4, 6-Trinitrophenol

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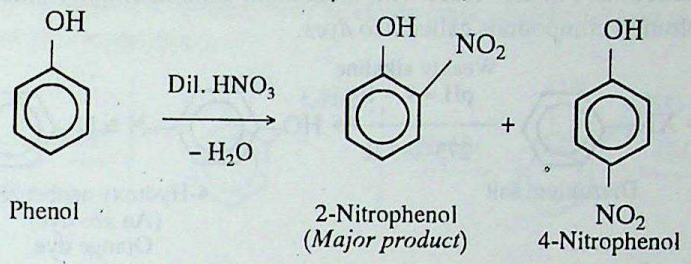
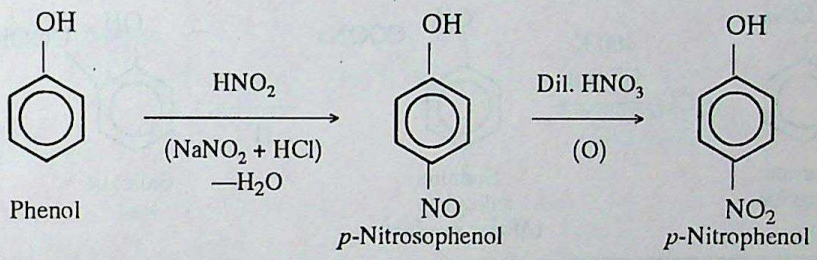
On treatment with dil. HNO_3 at low temperature (293 K), a mixture of *ortho* and *para* nitro phenols is formed.



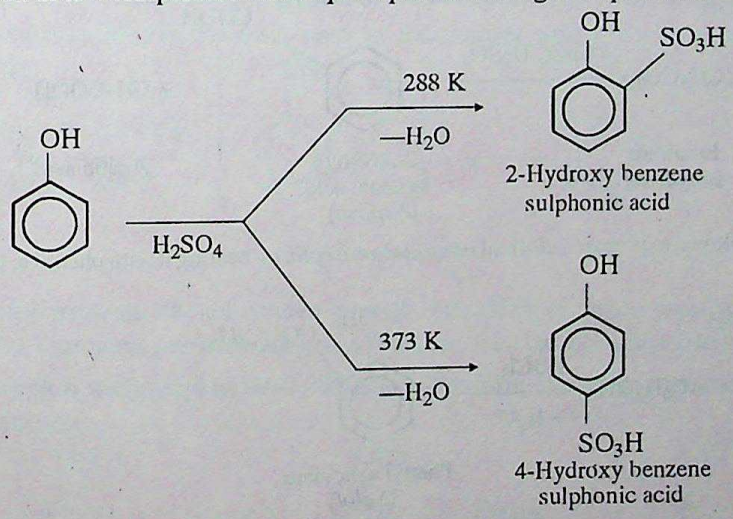
It must be noted that the yield of nitro product is low due to oxidation of ring by conc. HNO_3.

(*c*) **Nitrosation.** Phenol reacts with ice cold solution of nitrous acid (HNO_2) to form *p*-nitrosophenol. The *p*-nitrosophenol can be further oxidised with dilute HNO_3 to *p*-nitrophenol.

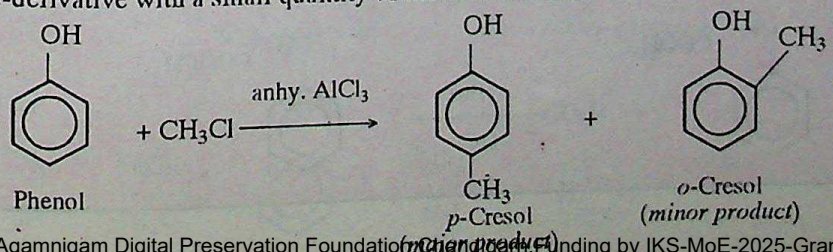


This reaction can be suitably employed to obtain more yield of nitro product.

(*d*) **Sulphonation.** Phenols are sulphonated with conc. H_2SO_4. Sulphonation takes place mainly at *ortho* position at low temperature and at *para* position at high temperature.



(*e*) **Friedel Craft alkylation.** Phenol reacts with alkyl halides in the presence of anhydrous $AlCl_3$ to form mainly *para*-derivative with a small quantity of the *ortho*-isomer.



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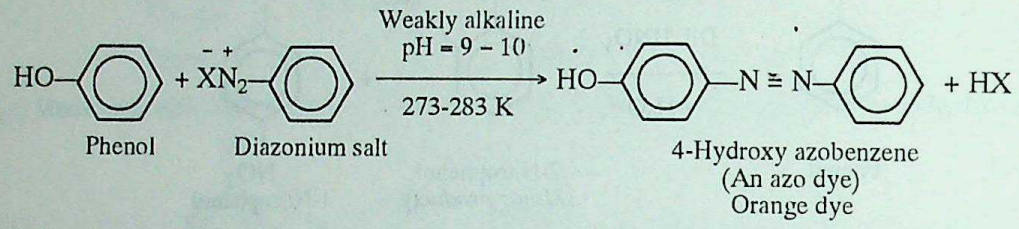
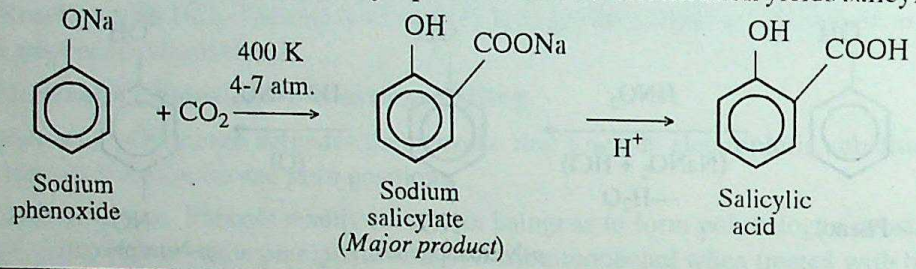
The yield of alkyl phenols is low because $AlCl_3$ reacts with phenol to produce a coordination compound.

(*f*) **Coupling Reaction.** Phenols react with diazonium salts in slightly alkaline medium and at low temperature to form coloured compounds called *azo dyes*.

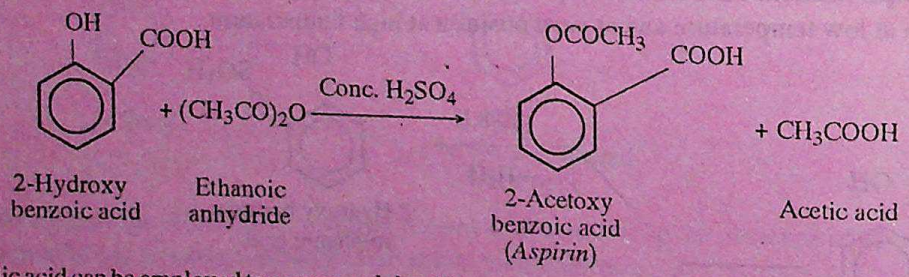


3. Some Special Reactions of Phenols

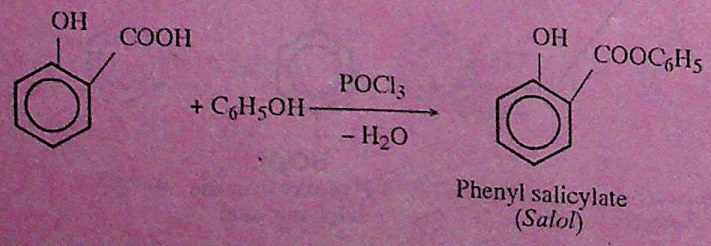
(*a*) **Kolbe's Reaction.** When sodium phenoxide is heated with CO_2 at 400 K and at a pressure of 4-7 atm. sodium salicylate is formed as the major product. This on acidification yields salicylic acid.



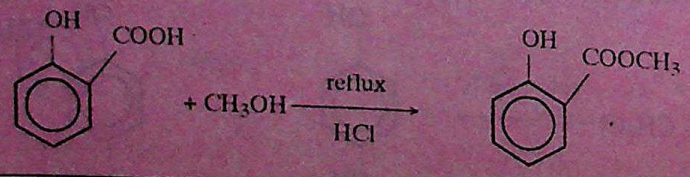
Salicylic acid is the starting material for the manufacture of 2-acetoxybenzoic acid (aspirin), the well known analgestic.



Salicylic acid can be employed to prepare *salol* and *intestinal antiseptic* by heating it with phenol in the presence of phosphoryl chloride



Methyl salicylate, a pleasant smelling liquid also called *oil of wintergreen*, is used in perfumery and as a flavouring agent can also be prepared from salicylic acid



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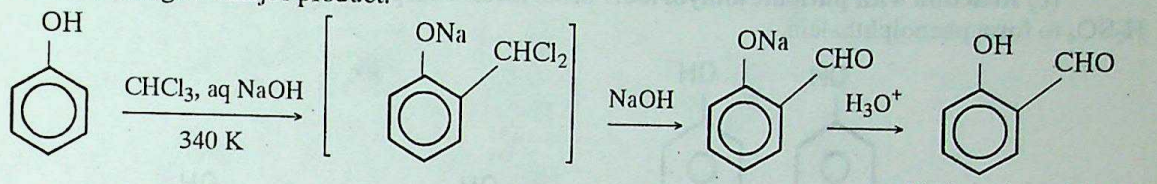
(*b*) **Reimer-Tiemann Reaction.** Treatment of phenol with chloroform in the presence of aqueous alkali at 340 K results in the formation of *o*-hydroxybenzaldehyde (salicyladehyde) and *p*-hydroxybenzaldehyde, the *ortho* isomer being the major product.

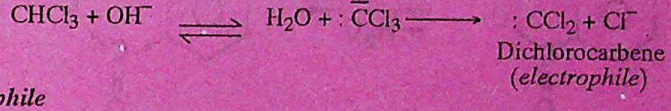


o-Hydroxy benzaldehyde
(*Major product*)

Mechanism

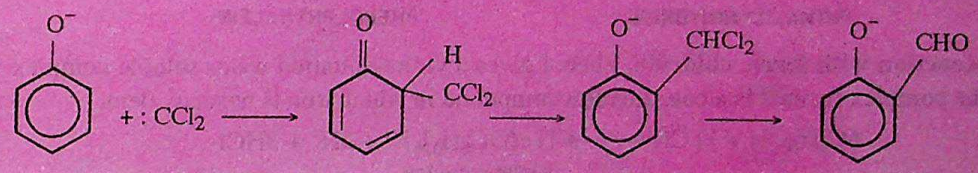
Reimer Tiemann reaction is an *electrophilic substitution* reaction. The reaction takes place through the following steps :

1. Generation of electrophile

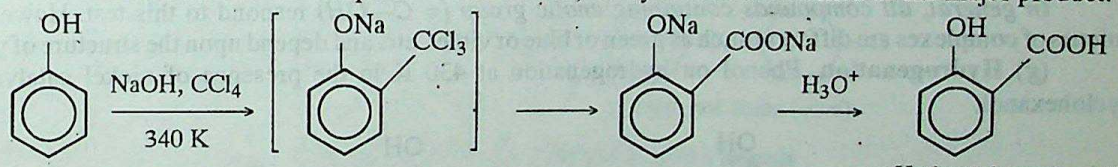


Dichlorocarbene
(*electrophile*)

2. Attack of electrophile



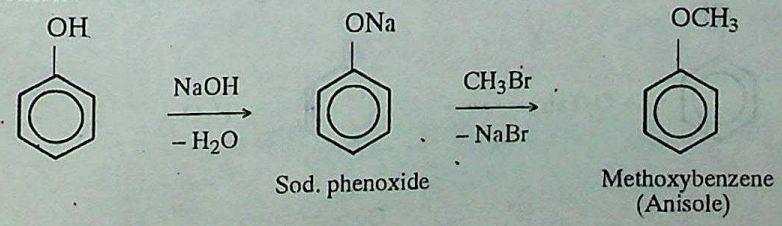
If carbontetrachloride is used in place of chloroform, salicylic acid is obtained as the major product.



o-Hydroxy benzoic acid
(Salicylic acid)
Major product

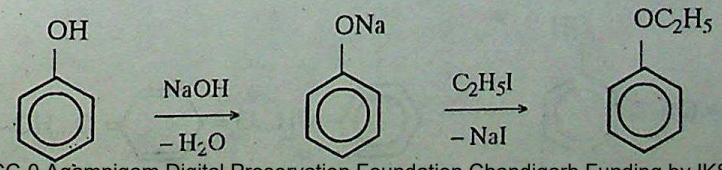
(*c*) **Condensation.** Phenol condenses with formaldehyde in the presence of dilute acid or alkali as a catalyst to yield a resinous substance bakelite. This reaction has been discussed in detail in *Section 14.4.2*.

(*d*) **Reaction with alkyl halides.** Phenols in the form of sodium phenoxide react with alkyl halides to form aromatic ethers.



Sod. phenoxide

Methoxybenzene
(Anisole)



Sodium phenoxide

Phenetole

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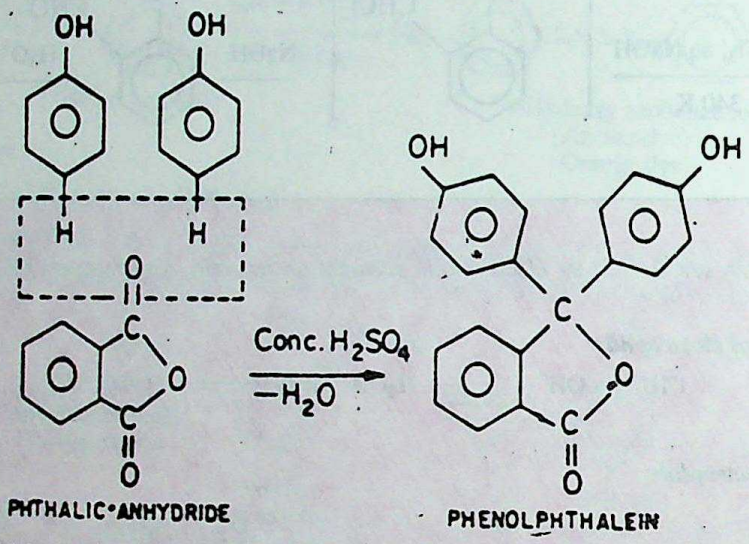
Unlike the reaction of alcohols, which is carried out in the presence of ether under anhydrous conditions, this reaction is carried out in aqueous medium.

(*e*) **Reaction with phthalic anhydride.** Phenol reacts with phthalic anhydride in the presence of conc. H_2SO_4 to form phenolphthalein.

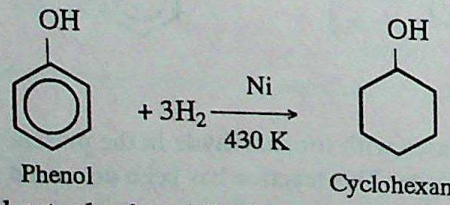


(*f*) **Reaction with ferric chloride.** Phenol gives a violet-coloured water soluble complex with ferric chloride. The complex formed is a coordination compound in which iron is hexacovalent.

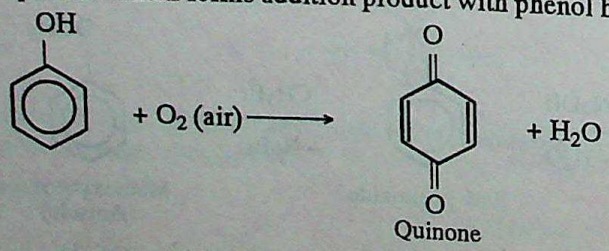
$$6C_6H_5OH + FeCl_3 \longrightarrow \underset{\text{Violet complex}}{[Fe(OC_6H_5)_6]^{3-}} + 3H^+ + 3HCl$$

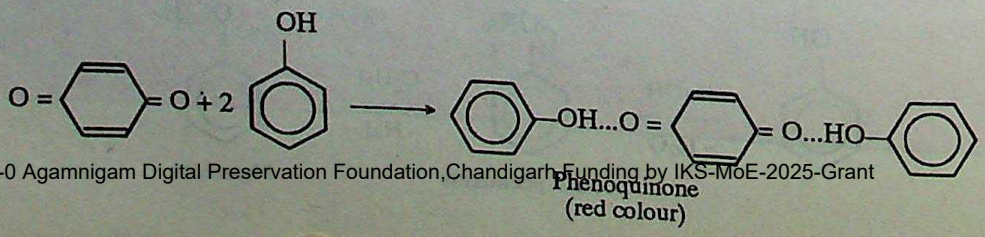
In general, all compounds containing enolic group (= $\overset{|}{C}$—*OH*) respond to this test. However, the colours of complexes are different such as green or blue or violet, etc. and depend upon the structure of phenols.

(*g*) **Hydrogenation.** Phenol on hydrogenation at 430 K in the presence of nickel catalyst gives cyclohexanol.



(*h*) **Oxidation.** Phenol gets slowly oxidised on exposure to air and turns pink in colour. One of the oxidation products in air is quinone which forms addition product with phenol having a red colour.





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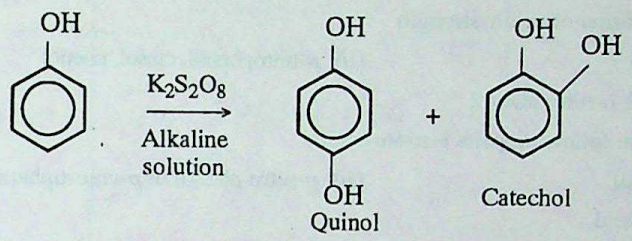
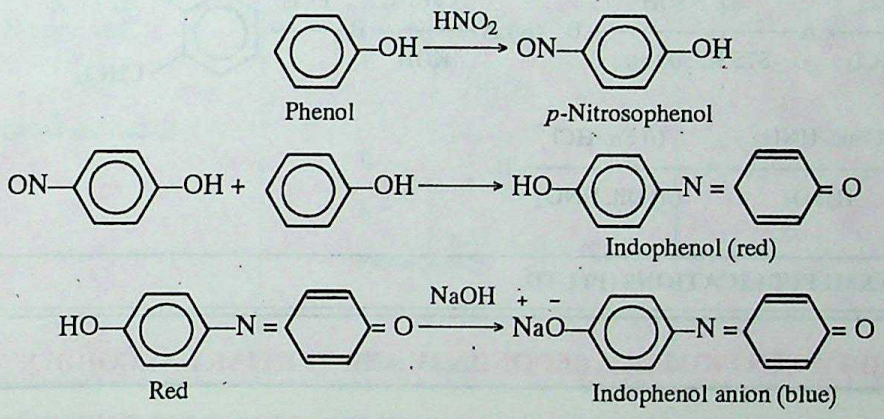
Monohydric phenols can also undergo oxidation with potassium persulphate in alkaline solution to give dihydric phenols.



This reaction is known as **Elbs-persulphate oxidation**.

(*i*) **Libermann's Test.** Most of the phenols give this test. Red or brown colouration is produced when a nitrite is added to a phenol dissolved in conc. sulphuric acid. The colour changes to blue or green by the addition of a strong alkali. This test can be used to distinguish phenols from alcohols.

$$\underset{\text{Sodium nitrite}}{2NaNO_2} + H_2SO_4 \longrightarrow \underset{\text{Nitrous acid}}{2HNO_2} + Na_2SO_4$$



Distinction between Alcohols and Phenols

Alcohols	*Phenols*
1. Alcohols do not have any effect on litmus solution.	1. Phenols turn blue litmus red.
2. Alcohols do not give any characteristic colour with $FeCl_3$ solution.	2. Phenols give characteristic colours such as violet, red, etc. with $FeCl_3$ solution.
3. Alcohols do not react with NaOH solution.	3. Phenols react with NaOH solution and form sodium salts.

REVIEW PROBLEMS

7.61. The two isomeric aromatic compounds A and B have formula C_7H_7OH. A gives purple colour with ferric chloride solution while B does not. Suggest the structures of A and B.

7.62. Out of *p*-cresol and *p*-xylene which can dissolve in aqueous KOH solution.

7.63. What is the main product formed when phenol is subjected to Kolbe's reaction.

7.64. Which is the strongest acid out of ethanol, 2-phenyl ethanol, phenol and 2, 4, 6-trinitrophenol.

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7.65. Which of the following can be used to distinguish between phenol and cyclohexanol : Na_2CO_3, NaOH, CH_3COCl ?

7.66. Arrange in the increasing order of acidic strength

(*i*) phenol, ethanol, water (*ii*) *p*-nitrophenol, cresol, phenol

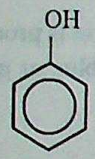
(*iii*) phenol, benzylalcohol, *o*-nitro phenol.

7.67. Which amongst each of the following pairs is more acidic

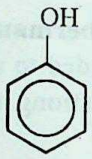
(*i*) phenol or cyclohexanol (*ii*) *p*-nitro phenol or *p*-chlorophenol

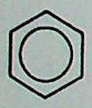
(*iii*) picric acid or formic acid.

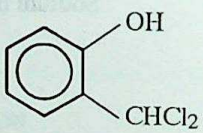
7.68. Complete the following equations supplying A and B :

(*i*) 

$\xrightarrow{\text{Zn dust}}$ A $\xrightarrow[\text{traces } SO_3]{H_2SO_4}$ B

(*ii*) A $\xrightarrow{\text{Sn/HCl}}$ B $\xrightarrow[\text{(ii) } H_2O]{\text{(i) } NaNO_2/HCl}$ 

(*iii*) 
$\xrightarrow[AlCl_3]{Cl_2}$ A $\xrightarrow[\text{575 K, 300 atm}]{\text{aq. NaOH}}$ B

(*iv*) A $\xrightarrow[KOH]{CHCl_3}$ B $\xrightarrow{PCl_5}$ 

(*v*)
$\xrightarrow[H_2SO_4]{\text{Conc. } HNO_3}$ A $\xrightarrow[\text{(ii) Dil. } HNO_2]{\text{(i) Sn/HCl}}$ B.

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7.19. DISTINCTION BETWEEN PRIMARY, SECONDARY AND TERTIARY ALCOHOLS

1. Lucas test. This test is based upon relative reactivities of various alcohols towards HCl in the presence of $ZnCl_2$. In this test, the alcohol is treated with Lucas reagent which is equimolar mixture of HCl and $ZnCl_2$. Alcohols are soluble in Lucas reagent and form a clear solution. On reaction, alkyl chlorides are formed which being insoluble result in cloudiness in the solution.

$$R—O—H + H—Cl \xrightarrow{ZnCl_2} R—Cl + H_2O$$

If cloudiness appears immediately, tertiary alcohol is indicated.

If cloudiness appears within five minutes, secondary alcohol is indicated.

If cloudiness appears only upon heating, primary alcohol is indicated.

2. Victor Meyer's test. In this test, the given alcohol is first converted into its iodide by treating it with HI or P/I_2. The alkyl iodide is then distilled with silver nitrite to convert it into nitroalkane. The nitroalkane is then treated with nitrous acid. The resulting solution is made alkaline with KOH and colour of the solution is observed.

If **blood red** *colour appears, it indicates a* **primary alcohol.**

If **blue colour** *appears, it indicates a* **secondary alcohol.**

If **colourless,** *it indicates a* **tertiary alcohol**

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Chemical reactions involved in the test are given below :

Primary alcohol	*Secondary alcohol*	*Tertiary alcohol*
$R—CH_2OH$ ↓ P/I_2 $R—CH_2I$ Alkyl iodide ↓ $AgNO_2$ $R—CH_2—NO_2$ ↓ HNO_2 $R—C(=N—OH)—NO_2$ Nitrolic acid ↓ KOH ***Blood red colour***	R_2CHOH ↓ P/I_2 R_2CHI Alkyl iodide ↓ $AgNO_2$ $R_2CH—NO_2$ ↓ HNO_2 $R_2C(N=O)—NO_2$ Pseudonitrol ↓ KOH ***Blue colour***	$R_3C—OH$ ↓ P/I_2 $R_3C—I$ ↓ $AgNO_2$ $R_3C—NO_2$ ↓ HNO_2 No action ↓ KOH ***Colourless***

7.20. SOME COMMERCIALLY IMPORTANT ALCOHOLS AND PHENOLS

1. Methanol. Methanol is a colourless liquid with boiling point 337 K. It is highly poisonous. Commercially, it is prepared by catalytic hydrogenation of carbon monoxide. Water gas (which is equimolar mixture of CO and H_2) is mixed with half of its volume with hydrogen gas and is compressed to 200 atmospheric pressure. The compressed gaseous mixture is then passed over a catalyst heated at 573 K. The catalyst consists of the oxides of copper, zinc and chromium.

$$CO + 2H_2 \xrightarrow[CuO—ZnO—Cr_2O_3]{573\ K,\ 200\ atm} CH_3OH$$

Methanol is also known as **wood-spirit** because earlier it was prepared by destructive distillation of wood.

Uses of Methanol

1. In the manufacture of formaldehyde and dimethyl terephthalate.
2. As aviation fuel.
3. Denaturant for ethyl alcohol.
4. Dehydrator for natural gas.
5. As automobile antifreeze.
6. Solvent for nitro cellulose, resin, dyes, plastics, paints and varnishes.

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2. Ethanol. Ethanol is a colourless liquid with boiling point 351.3 K. It is prepared on large scale by hydration of ethene and fermentation of carbohydrates (*Section 7.12*). It is also known as **grain alcohol** as it is manufactured from starch grains.

Fermentation of carbohydrates yields ethanol containing water. This solution on fractional distillation forms an azeotrope containing 95 per cent ethanol and 5 per cent water. Thus, by simple fractional distillation we can get, at the most, a solution containing 95 per cent ethanol. This 95 per cent ethanol is known as **rectified spirit.**

Absolute alcohol is 100 per cent ethanol. As already mentioned, simple fractional distillation yields a constant boiling azeotropic mixture containing 95 per cent ethanol and 5 per cent water. Absolute alcohol can be obtained by adding small amount of benzene to the rectified spirit and then distilling. The first fraction is an azeotropic mixture of water, ethanol and benzene (b.p. 337.8 K). This removes water completely. The second fraction is an azeotropic mixture of benzene and ethanol (b.p. 341.2 K). This removes benzene completely. Finally, pure ethanol or absolute alcohol distills over at 351.3 K.

Ethyl alcohol in the form of alcoholic beverages is used for drinking. The alcohol used for drinking is heavily taxed in the form of excise duty. However, alcohol used for industrial purposes is not taxed. To prevent the misuse, the industrial alcohol is made unfit for drinking by addition of 5—10 per cent methanol. The ethanol denaturated by methanol (and a little of pyridine and acetone), is called **methylated spirit.**

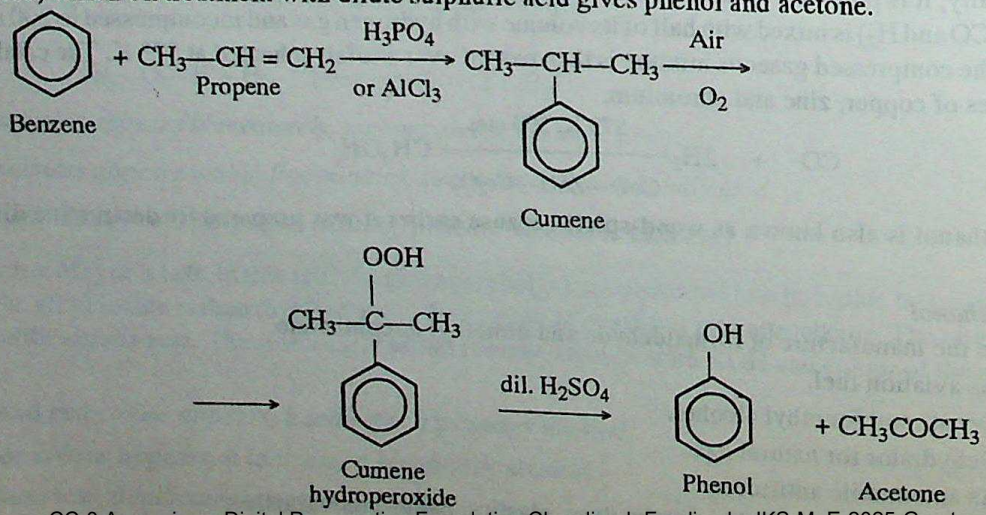
Ethyl alcohol may also be mixed with petrol. A mixture of 20% ethanol and 80% gasoline is used in internal combustion engines. Since alcohol does not mix with petrol therefore a third solvent benzene or ether or tetralin (tetra hydronapthalene) is used as a solvent. Ethyl alcohol used for the purpose of generation of power in internal combustion engine is called **power alcohol.**

Uses of Ethanol

1. In the manufacture of dyes, synthetic drugs and detergents.
2. In explosives, surface coatings and cosmetics.
3. As a beverage.
4. As antifreeze.
5. As a solvent for resins, fats, oils, fatty acids and hydrocarbons.

3. Phenol

The starting material for the preparation of phenol is cumene (isopropyl benzene). Cumene itself is prepared by Friedel-Craft alkylation of benzene with propene. Cumene is oxidised by air to cumene hydroperoxide, which on treatment with dilute sulphuric acid gives phenol and acetone.



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Uses of Phenol

1. In the manufacture of drugs like salicylic acid, phenacetin, aspirin, salol, etc.
2. For the manufacture of bakelite by polymerising with formaldehyde.
3. For the manufacture of phenolphthalein, picric acid.
4. As a preservative for ink.
5. For the manufacture of cyclohexanol used as solvent for rubber.
6. As a powerful antiseptic in soaps, lotions, etc.

4. 1, 2-Ethanediol (Ethylene glycol)

Methods of Preparation·

1. From ethene. (*i*) In laboratory, ethylene glycol is prepared by the action of alkaline solution of potassium permanganate on ethene.

$$3CH_2 = CH_2 + 2KMnO_4 + 4H_2O \longrightarrow 3\underset{OH}{\underset{|}{CH_2}}—\underset{OH}{\underset{|}{CH_2}} + 2MnO_2 + 2KOH$$

1, 2-Ethanediol

(*ii*) Commercially, it is prepared by oxidation of ethene to epoxy-ethane, which is subsequently hydrolysed with superheated steam.

$$CH_2 = CH_2 + \frac{1}{2}O_2 \xrightarrow[475—675\ K]{Ag} \underset{O}{CH_2—CH_2} \xrightarrow[H_2O]{473\ K} \underset{OH}{\underset{|}{CH_2}}—\underset{OH}{\underset{|}{CH_2}}$$

Epoxyethane

2. From oxalic esters. Oxalic esters on reduction with sodium and alcohol give ethylene glycol.

$$\underset{COOC_2H_5}{\underset{|}{COOC_2H_5}} + 8H \xrightarrow{Na/C_2H_5OH} \underset{CH_2OH}{\underset{|}{CH_2OH}} + 2C_2H_5OH$$

Diethyl exalate

3. From ethylene diamine. Ethylene diamine on reaction with nitrous acid gives ethylene glycol.

$$\underset{CH_2NH_2}{\underset{|}{CH_2NH_2}} + 2HNO_2 \longrightarrow \underset{CH_2OH}{\underset{|}{CH_2OH}} + 2H_2O + 2N_2$$

Physical Properties. (1) Ethylene glycol is a colourless, syrupy liquid with a high b.p. (470 K).

(2) It is miscible with water in all proportions. It forms low freezing mixtures with water and is therefore used as antifreeze.

Chemical Properties. Ethylene glycol contains two primary —OH groups and hence ***it exhibits general chemical properties of primary alcohols.*** The reaction of first —OH group occurs with ease while those of the second —OH group sometimes require vigorous conditions. Some of the characteristic reactions of ethylene glycol are given below :

1. Reaction with sodium. Sodium reacts with ethylene glycol at 325 K to form monosodium glycolate. However, at 430 K it gives disodium glycolate.

$$\underset{CH_2OH}{\underset{|}{CH_2OH}} \xrightarrow[325\ K,\ -\frac{1}{2}H_2]{Na} \underset{CH_2OH}{\underset{|}{CH_2ONa}} \xrightarrow[430\ K,\ -\frac{1}{2}H_2]{Na} \underset{CH_2ONa}{\underset{|}{CH_2ONa}}$$

Mono-sodium glycolate — Disodium glycolate

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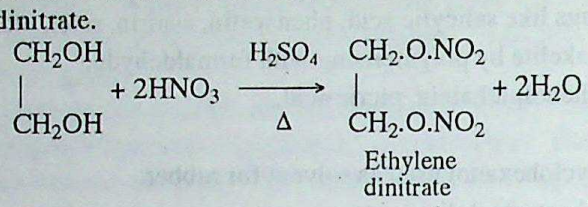
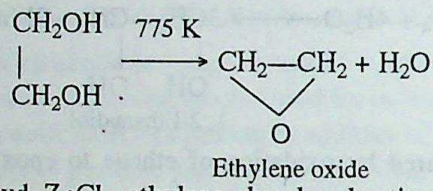
2. Reaction with nitric acid. When heated with conc. HNO_3 in the presence of conc. H_2SO_4, ethylene glycol gives ethylene dinitrate.



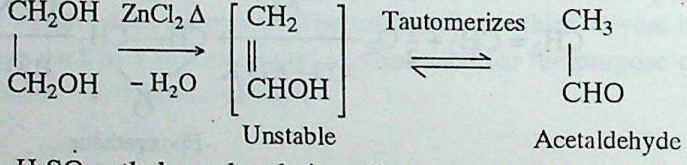
3. Reaction with phthalic acid. On reaction with phthalic acid and other dibasic acids, ethylene glycol forms polyesters, known as *Alkyd polymers*. These are discussed in *Section 14.2.2*.

4. Dehydration. Under different conditions, ethylene glycol undergoes dehydration in different ways :

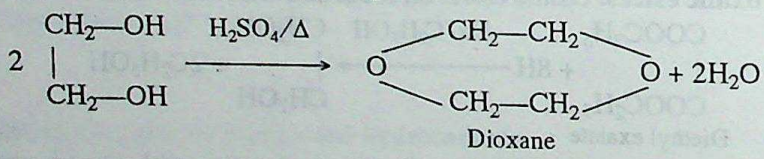
(*i*) When heated alone at about 775 K, it forms ethylene oxide,



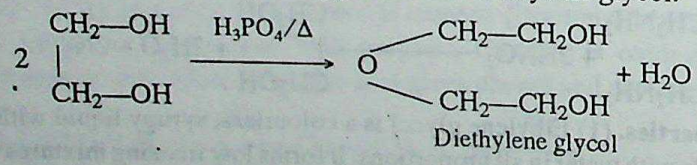
(*ii*) In the presence of anhyd. $ZnCl_2$, ethylene glycol on heating gives acetaldehyde.



(*iii*) On heating with conc. H_2SO_4, ethylene glycol gives dioxane.

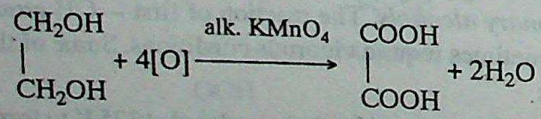


(*iv*) When heated with conc. H_3PO_4, ethylene glycol forms diethylene glycol.

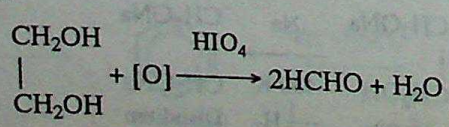


5. Oxidation. Ethylene glycol on oxidation with different oxidizing agents gives different products.

(*i*) With dil. HNO_3 or alkaline $KMnO_4$, it gives oxalic acid.



(*ii*) When periodic acid (HIO_4) or lead tetra acetate is used, carbon-carbon bond undergoes cleavage and formaldehyde is formed.



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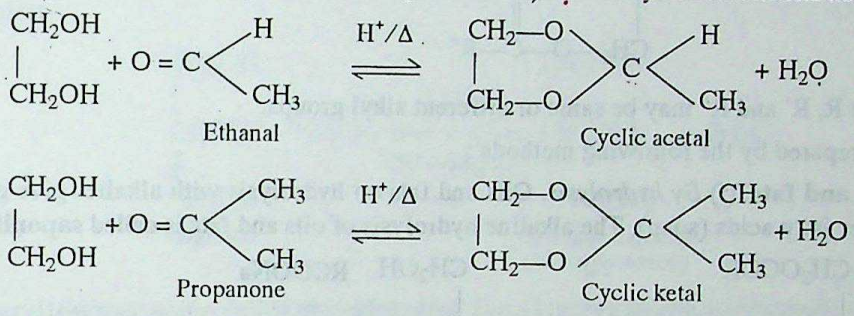
(*iii*) When acidified $KMnO_4$ or acidified $K_2Cr_2O_7$ is used, carbon-carbon bond undergoes cleavage and formic acid is formed.

$$\begin{array}{l} CH_2OH \\ | \\ CH_2OH \end{array} + 3[O] \xrightarrow{KMnO_4/H^+} 2HCOOH + H_2O$$

6. Reaction with aldehydes and ketones. Ethylene glycol reacts with aldehydes and ketones in the presence of mineral acids or PTS (*p*-Toluene sulphonic acid) to form cyclic acetals and ketals (1, 3-dioxalones).



Uses of 1, 2-Ethanediol

1. As an antifreeze in automobile radiators.
2. As a coolant for aeroplane engines.
3. In the manufacture of terylene.
4. As a solvent and preservative.
5. In organic synthesis.

REVIEW PROBLEMS

7.69. Transform the following compounds to ethylene glycol

(*i*) oxirane (*ii*) cyanogen (*iii*) glyoxal (*iv*) oxalyl chloride.

7.70. Complete the following reactions :

(*i*) $CH_2 = CH_2 \xrightarrow[CS_2]{Cl_2} ? \xrightarrow{aq.\ KOH} ?$ (*ii*) $? \xrightarrow{H_2O/HCl} ? \xrightarrow{ZnCl_2} CH_3CHO$

(*iii*) $? \xrightarrow[ZnCl_2]{anhy} ? \xrightarrow[H_2SO_4]{(CH_2)_2(OH)_2} CH_3CH\begin{array}{l} O—CH_2 \\ | \\ O—CH_2 \end{array}$

7.71. What is an antifreeze ? Give one example.

7.72. Name one polymer that is formed by ethylene glycol.

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5. 1, 2, 3-Propanetriol (Glycerol or Glycerine)

Glycerol is a colourless, odourless syrupy liquid having sweet taste. It has high boiling point (563 K). It is soluble in water in all proportions.

Glycerol occurs in nature in oils and fats. Oils and fats are triesters of glycerol with higher fatty acids. These triesters are called glycerides. The higher fatty acid may be such as palmitic acid ($C_{15}H_{31}COOH$), or stearic acid ($C_{17}H_{35}COOH$). A glyceride may be represented by general formula given below :

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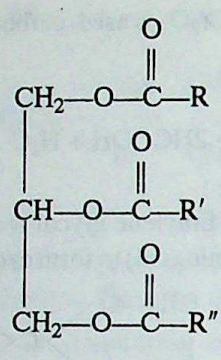
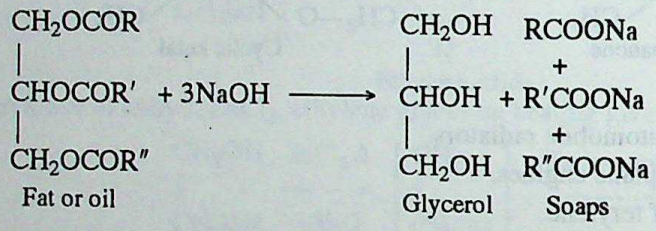


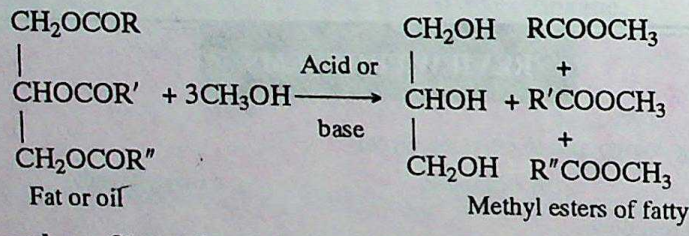
In a glyceride R, R′ and R″ may be same or different alkyl groups.

Glycerol is prepared by the following methods :

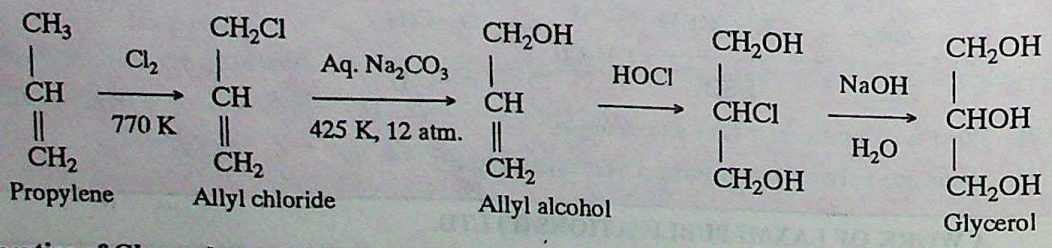
1. **From oils and fats.** (*i*) *By hydrolysis*. Oils and fats on hydrolysis with alkalies give glycerol and sodium salts of higher fatty acids (soap). The alkaline hydrolysis of oils and fats is called **saponification**.



(*ii*) *By trans-esterification*. Oils and fats on refluxing with methyl alcohol in the presence of acid or base undergo trans-esterification whereby glycerol is set free.



2. **From propylene.** Glycerol can also be obtained from propylene by hydration. Propylene itself is obtained by cracking of petroleum. The various steps involved in the conversation of propylene into glycerol are given below.



Physical Properties of Glycerol

1. Glycerol is a colourless and odourless syrupy liquid having sweet taste.
2. It boils at 563 K.
3. On cooling, glycerol forms tansparent solid crystals which melt at 290 K.
4. It is soluble in water in all proportions.
5. Impure glycerol can be purified by distillation with super heated steam under reduced pressure.

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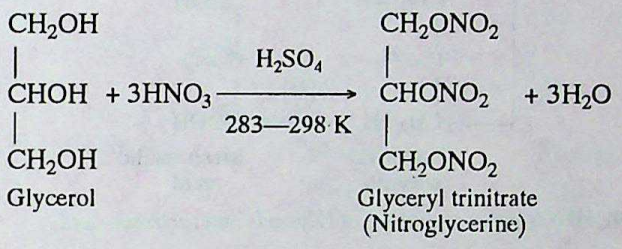
Chemical Properties of Glycerol

Glycerol contains two types of —OH group *i.e.*, primary and secondary alcoholic group. It undergoes all reactions characteristic of these groups. In addition, it also undergoes some reactions typical of polyhydric alcohols.

Some important reactions of glycerol are :

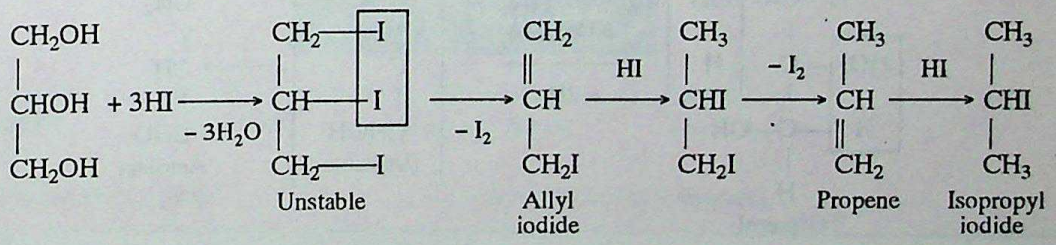
1. **Nitration.** Glycerol reacts with mixture of conc. HNO_3 and conc. H_2SO_4 at 283-298 K to form glyceryl trinitrate.



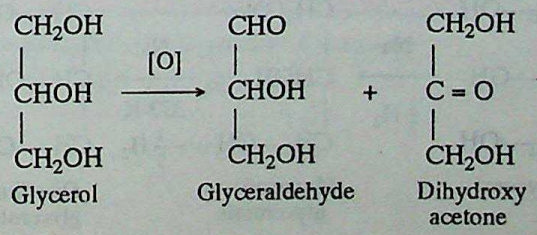
Glyceryl trinitrate is also called **nitroglycerine**. It is a highly explosive substance. A mixture of glyceryl trinitrate and glyceryl dinitrate adsorbed on *kieselguhr* (a kind of porous earth) is called **dynamite**. Dynamite was discovered by Alfred Nobel. (Nobel Prizes are named after Alfred Nobel). Dynamite is used for rock blasting and for making bombs.

Glyceryl trinitrate is also used as medicine to lower blood pressure.

2. **Reaction with hydrogen iodide.** When glycerol is warmed with small amount of hydrogen iodide allyl iodide is formed. However, on heating with excess of hydrogen iodide the product obtained is isopropyl iodide.



3. **Reaction with Fenton's reagent.** Glycerol is oxidised with mild oxidizing agents such as Fenton's reagent ($FeSO_4 + H_2O_2$). On oxidation, a mixture of glyceraldehyde and dihydroxy acetone is obtained. The mixture is called as **gylcerose**.



Stronger oxidizing agents can finally oxidize glycerol to carbon dioxide and water.

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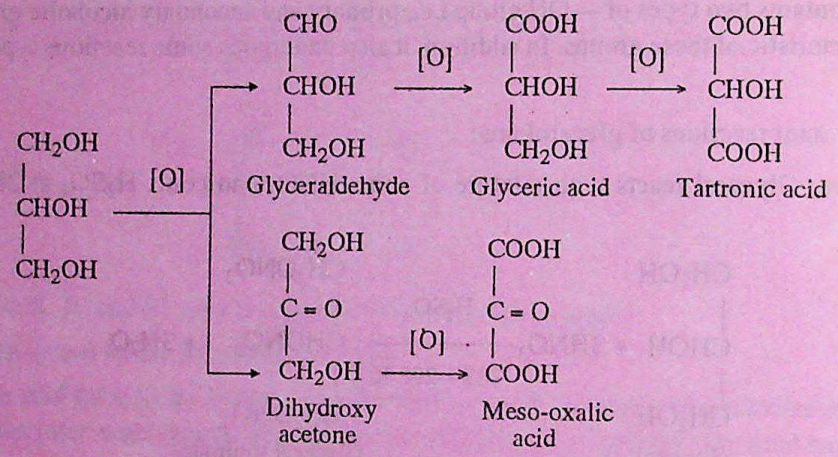
Other Oxidation Reactions of Glycerol. A large number of products can be obtained by oxidation of glycerol. The stepwise oxidation is as shown beneath.



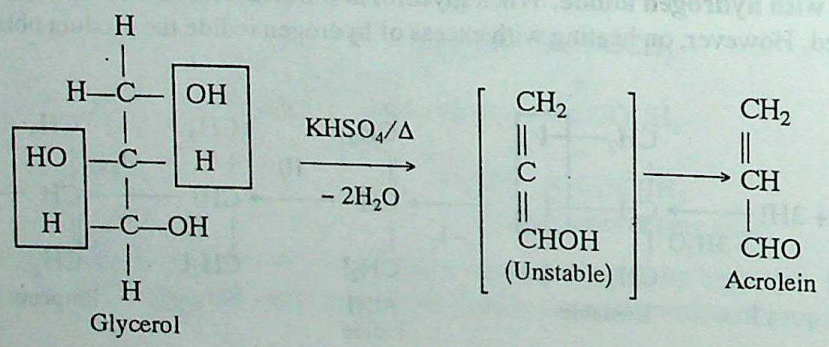
(*i*) Oxidation with dil. HNO_3 gives a mixture of *Glyceric* and *tartronic acid.*

(*ii*) Oxidation with conc. HNO_3 gives *glyceric acid.*

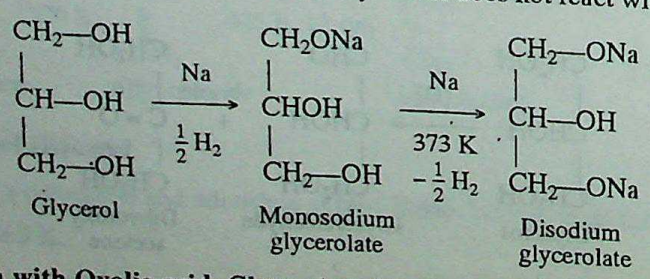
(*iii*) Oxidation with bismuth nitrate gives *meso oxalic acid.*

(*iv*) Oxidation with mild oxidising agents like bromine water, sodium hypobromite (Br_2/NaOH) gives a mixture of *glyceraldehyde and dihydroxy acetone.*

4. Dehydration. Glycerol undergoes dehydration on heating with $KHSO_4$ and results in the formation of an unsaturated aldehyde, acrolein.



5. Reaction with sodium. At room temperature, sodium reacts with one of the primary —OH groups of glycerol to form monosodium derivative. However, at higher temperature (373 K) both the primary —OH groups react to form disodium derivative. Secondary —OH does not react with sodium.



6. Reaction with Oxalic acid. Glycerol on heating with oxalic acid at 383 K forms glycerol mono formate which on hydrolysis produces formic acid.

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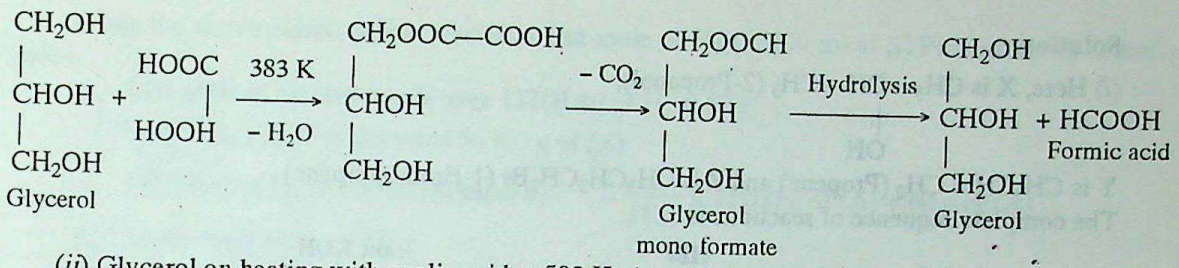
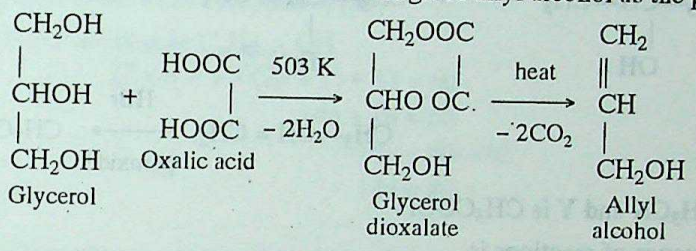


(*ii*) Glycerol on heating with oxalic acid at 503 K gives allyl alcohol as the product.



Uses of Glycerol

1. In the manufacture of nitro glycerine which is used as an explosive.
2. As a sweetening agent in confectionary and beverages.
3. As a lubricant for watches and clocks.
4. As an antifreeze in automobiles.
5. In the manufacture of cosmetics and transparent soaps.
6. In the preparation of organic compounds such as allyl alcohol, formic acid, etc.
7. It is used in the manufacture of alkyl resins.

REVIEW PROBLEMS

7.73. What happens when glycerol is treated with the following. Name the products :
(*i*) $NaHSO_4$ (*ii*) OsO_4 (*iii*) conc. HNO_3 (*iv*) PCl_5.

7.74. Convert :
(*i*) allylalcohol to glycerol (*ii*) oxalic acid to formic acid.

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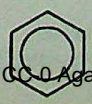
SOME MISCELLANEOUS PROBLEMS

Example 7.1. *Predict X, Y, Z in the following sequence of reactions :*

(*i*) $X \xrightarrow{HBr} CH_3-\underset{\underset{Br}{|}}{CH}-CH_3 \xrightarrow{alc.\ KOH} Y \xrightarrow[peroxide]{HBr} Z$

(*ii*) $CH_3Br \xrightarrow{KCN} X \xrightarrow{H_3O^+} Y$

(*iii*)  $\xrightarrow{Cl_2/FeCl_3} X \xrightarrow{CuCN} Y \xrightarrow{dil.\ HCl} Z$

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Solution.

(*i*) Here, X is $CH_3—\underset{\underset{OH}{|}}{CH}—CH_3$ (2-Propanol),

Y is $CH_3CH = CH_2$ (Propene) and Z is $CH_3CH_2CH_2Br$ (1-Bromopropane)

The complete sequence of reactions is

$$CH_3—\underset{\underset{OH}{|}}{CH}—CH_3 \xrightarrow{HBr} CH_3—\underset{\underset{Br}{|}}{CH}—CH_3 \xrightarrow{\text{alc. KOH}}$$

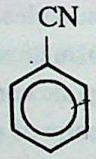
$$CH_3—CH = CH_2 \xrightarrow[\text{peroxide}]{HBr} CH_3CH_2CH_2Br$$

(*ii*) Here, X is CH_3CN and Y is CH_3COOH

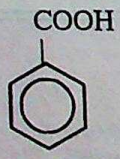
The complete sequence of reactions is

$$CH_3Br \xrightarrow{KCN} \underset{\text{Ethane nitrile}}{CH_3CN} \xrightarrow{H_3O^+} \underset{\text{Ethanoic acid}}{CH_3COOH}$$

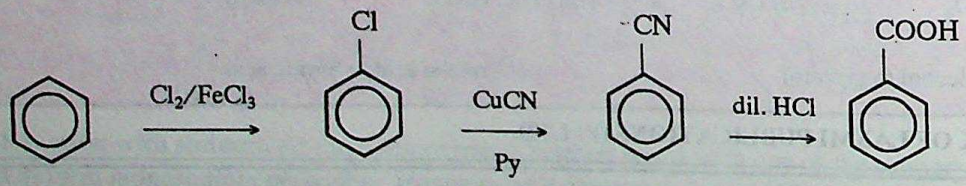
(*iii*) Here, X is

(Chlorobenzene) ; Y is 

(Phenylcyanide) and

Z is 

(Benzoic acid).



Example 7.2. *Compound (A) gives positive Lucas test in 5 minutes. When 6.0 g of (A) is treated with sodium metal, 1120 ml of hydrogen is evolved at STP. Assuming (A) to contain one atom of oxygen per molecule, write the structural formula of (A).*

Compound (A) when treated with PBr_3, gives compounds (B) which when treated with benzene in the presence of aluminium chloride gives compound (C). Write down the structural formula of (B) and (C).

(Roorkee Ent. 1990)

Solution.

Since compound (A) gives positive Lucas test in 5 minutes, it is a secondary alcohol.

I. *Calculation of molecular mass of the alcohol*

$$2\ —\overset{|}{\underset{|}{C}}—OH + 2Na \longrightarrow 2\ —\overset{|}{\underset{|}{C}}—ONa + H_2$$

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From the above equation it is clear that one mole of H_2 (22400 ml at STP) is given by 2 moles of alcohol.

∴ One mole of alcohol would give 11200 ml of H_2 at STP.

1120 ml of H_2 at STP is liberated by 6.0 g of (A)

∴ 11200 ml of H_2 would be liberated by $= \frac{6}{1120} \times 11200$ g of (A) = 60 g of (A)

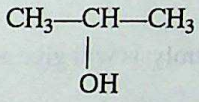
∴ Molar mass of (A) = 60 g.

II. *Determination of structural formula of (A)*

Let the formula of alcohol be $C_nH_{2n+1}OH$

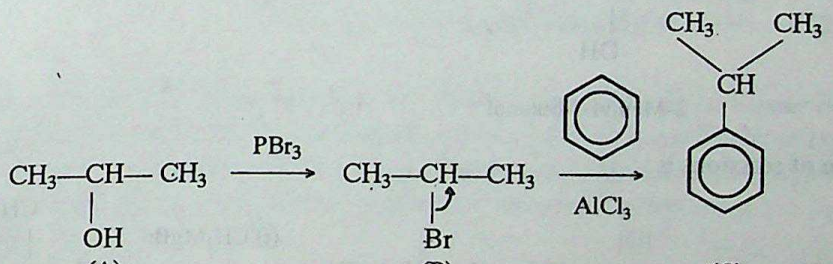
$$12 \times n + 1 \times (2n + 1) + 17 = 60$$
$$14n + 18 = 60$$
$$14n = 60 - 18$$
$$14n = 42$$
$$n = 3$$

From this it follows that alcohol contains three carbon atoms and had molecular formula C_3H_7OH. The secondary alcohol of three carbon atoms containing only one oxygen atom is



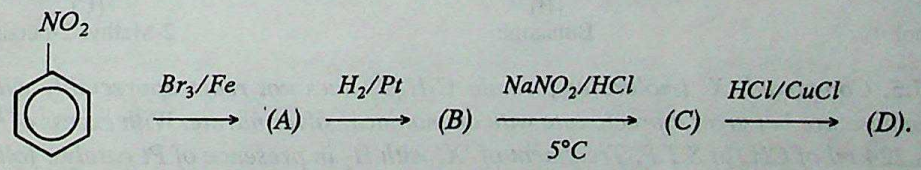
2-Propanol

The sequence of reactions (A) to give (B) and (C), and the structural formulae of (B) and (C) are given below :

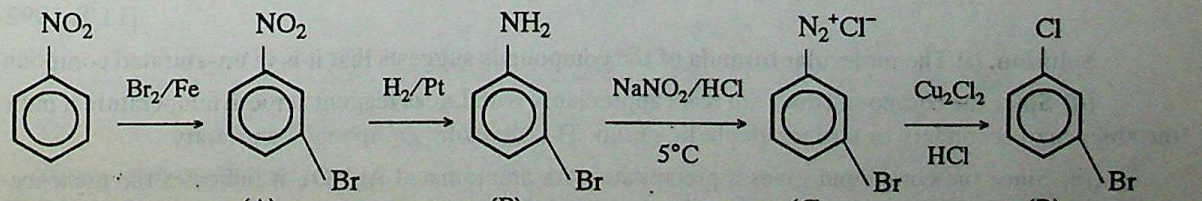


(A) (B) 2-Bromopropane (C) Isopropyl benzene

Example 7.3. *Complete the following supplying (A), (B), (C) and (D) :*



Solution.



(A) 3-Bromonitroaniline (Nitro group is *m*-directing) (B) 3-Bromoaniline (C) (D) 3-Bromochlorobenzene

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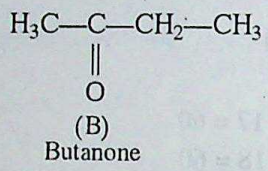
Example 7.4. *A compound (A) with molecular formula $C_4H_{10}O$ on oxidation forms compound (B). The compound (B) gives positive iodoform test. Compound (B) on reaction with CH_3MgBr followed by hydrolysis gives (C). Identify (A), (B) and (C), and give the sequence of reactions.*

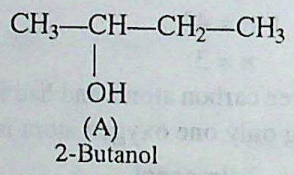
Solution.

Since (B) gives positive iodoform test it must be a methyl ketone. The only methyl ketone with four carbon atoms is



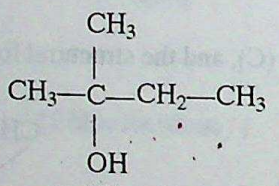
(B)
Butanone

Butanone will be obtained by oxidation of 2-butanol. Hence (A) is 2-butanol



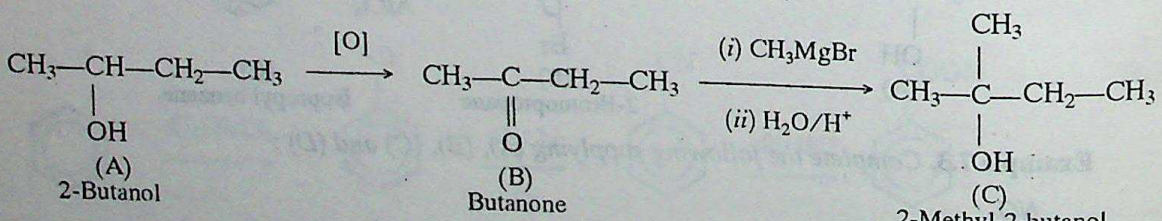
(A)
2-Butanol

Butanone on reaction with CH_3MgBr followed by hydrolysis will give a tertiary alcohol



(C)
2-Methyl-2-butanol

The sequence of reactions is



(A) 2-Butanol → (B) Butanone → (C) 2-Methyl-2-butanol

Example 7.5. *Compound 'X' (molecular formula C_5H_8O) does not react appreciably with Lucas reagent at room temperature but gives a precipitate with ammoniacal silver nitrate. With excess of MeMgBr 0.42 g of 'X' gives 224 ml of CH_4 at S.T.P. Treatment of 'X' with H_2 in presence of Pt catalyst followed by boiling with excess HI gives n-pentane. Suggest structure for 'X' and write the equations involved.*

[I.I.T. 1992 (5)]

Solution. (*i*) The molecular formula of the compounds suggests that it is in unsaturated compound.

(*ii*) Since the compound does not react appreciably with Lucas reagent at room temperature it indicates the absence of secondary or tertiary alcoholic group. The alcoholic group may be primary.

(*iii*) Since the compound gives a precipitate with ammoniacal $AgNO_3$, it indicates the presence of a terminal triple bond.

(*iv*) Molecular mass of 'X' is 84.

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Volume of methane liberated at S.T.P. by 1 mole of 'X' is

$$= \frac{224}{0.42} \times 84 = 2 \times 22400 \text{ mL}$$

2×22400 mL of methane = 2 moles of methane

Thus, 1 mole of 'X' on reaction with excess MeMgBr liberates 2 mole of methane. This indicates that there are two acidic hydrogen atoms in a molecule of 'X'. One of these is as terminal triple bond, the other must be as primary—OH group.

(*v*) Treatment of 'X' with H_2 in the presence of Pt followed by boiling with excess HI gives *n*-pentane. It indicates that 'X' contains a straight chain of five carbon atoms.

On the basis of the above observations of compound 'X' may be assigned the following structure :

$$H—C \equiv C—CH_2—CH_2—CH_2—OH$$

Equations involved in the above reactions are follows :

$$HC \equiv CCH_2CH_2CH_2OH \xrightarrow{2CH_3MgBr} BrMg—C \equiv C—CH_2CH_2CH_2OMgBr + 2CH_4$$

$$HC \equiv CCH_2CH_2CH_2OH \xrightarrow[NH_4OH]{AgNO_3} \underset{\text{White ppt}}{AgC \equiv C—CH_2CH_2CH_2OH}$$

$$HC \equiv CCH_2CH_2CH_2OH \xrightarrow[Pt]{+2H_2} CH_3CH_2CH_2CH_2CH_2OH \xrightarrow{HI} \underset{n\text{-Pentane}}{CH_3CH_2CH_2CH_2CH_3}$$

Example 7.6. *An organic compound [A] has 76.6% C and 6.38% H. Its vapour density is 47. It gives characteristic colour with aq. $FeCl_3$ solution. [A] when treated with CO_2 and NaOH at 140°C under pressure gives [B] which on being acidified gives [C]. [C] reacts with acetyl chloride to give [D] which is a well known pain killer. Identify [A], [B], [C] and [D] and explain the reactions involved.*

Solution.

Calculation of empirical and molecular formula of the compound

Element	*Percentage*	*Relative no. of atoms*	*Simplest whole no. of ratio of atoms*
C	76.6%	$\frac{76.6}{12} = 6.38$	6
H	6.38%	$\frac{6.38}{1} = 6.38$	6
O	17.02%	$\frac{17.02}{16} = 1.06$	1

Empirical formula of the compound $= C_6H_6O$

Empirical formula mass $= 12 \times 6 + 1 \times 6 + 16 = 94$

Molecular mass $= 2 \times$ V.D.

$= 2 \times 47 = 94$

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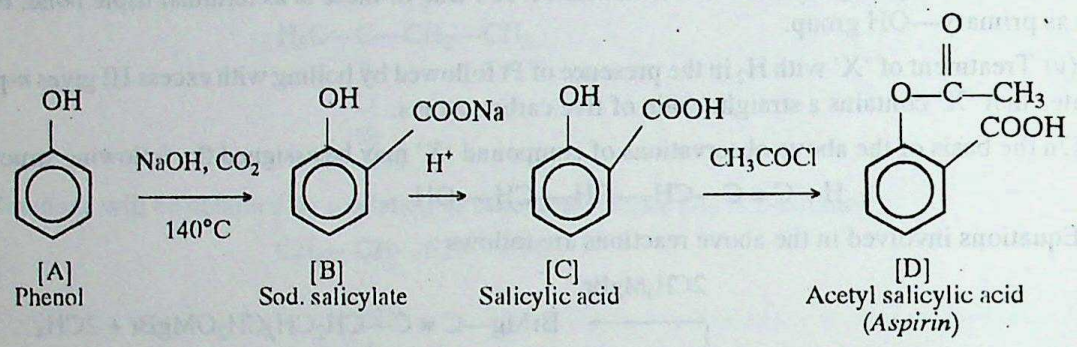
Since molecular mass of the compound is equal to its empirical formula mass therefore molecular formula of the compound is same as its empirical formula, *i.e.* C_6H_6O.

Since the compound gives characteristic colour with aq. $FeCl_3$ solution it must be a phenol. Phenol on reaction with CO_2 and NaOH at 140°C would undergo Kolbe reaction to form sodium salicylate (B), which on acidification would yield salicylic acid (C). Salicylic acid on reaction with acetyl chloride would undergo acylation to yield acetyl salicylic acid, (D).



Example 7.7. *0.37 g of an alcohol was added to CH_3MgI and the gas evolved measured 112 cm^3 at STP. What is the molecular weight of ROH ? On dehydration, ROH gives an alkene which on ozonolysis gives acetone as one of the products. ROH on oxidation easily gives an acid containing the same number of carbon atoms. Give structures of ROH and the acid with proper reasoning.* (Roorkee Ent. 1994)

Solution.

$$ROH + CH_3MgI \longrightarrow Mg\begin{matrix} I \\ OR \end{matrix} + CH_4$$

From the equation, it is clear that moles of methane produced is equal to the moles of ROH.

$$\text{Moles of ROH} = \frac{0.37}{M}$$

where M is the molecular mass of ROH

$$\text{Moles of } CO_2 = \frac{112}{22400}$$

$$\frac{0.37}{M} = \frac{112}{22400}$$

$$M = \frac{22400 \times 0.37}{112} = 74$$

Thus, molecular mass of ROH = 74

Let the molecular formula of the alcohol be $C_nH_{2n+1}OH$

$$12 \times n + 1 \times (2n + 1) + 17 = 74$$

$$14n + 1 + 17 = 74$$

$$14n = 74 - 18 = 56$$

$$n = 4$$

∴ Molecular formula of ROH = C_4H_9OH

Since on oxidation the alcohol gives an acid with same number of carbon atoms, the alcohol must be **a primary alcohol.**

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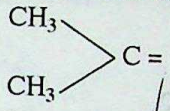
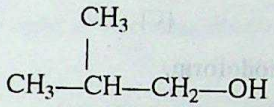
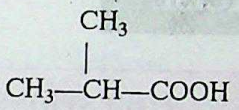
Since the dehydration product of ROH on ozonolysis gives acetone as one of the products, the alkene formed must have the group



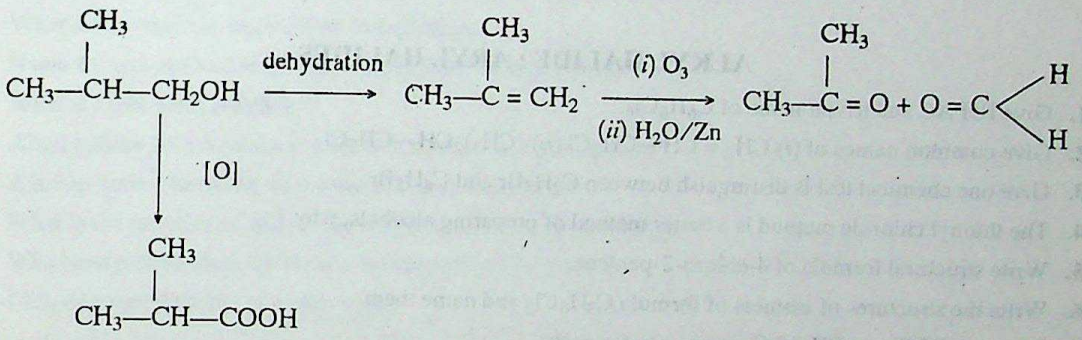
From this information the structure of the alcohol may be written as



This alcohol on oxidation would give acid :

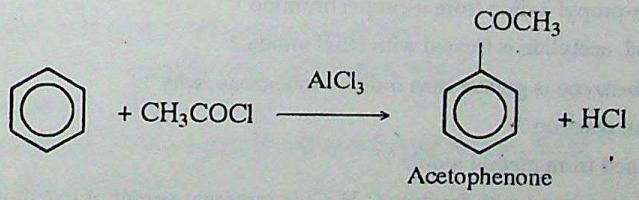


The reactions involved are given below :



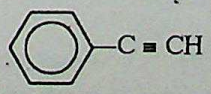
Example 7.8. *An organic compound A, C_8H_6 on treatment with dilute sulphuric acid containing mercuric sulphate gives a compound B, which can also be obtained from a reaction of benzene with an acid chloride in the presence of anhydrous aluminium chloride. The compound B, when treated with iodine in aqueous KOH, yields C and a yellow compound D. Identify A, B, C and D with justification. Show how B is formed from A.* [I.I.T. 1994 (5)]

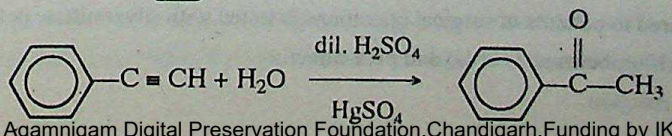
Solution. Reaction of CH_3COCl with benzene in the presence of $AlCl_3$ would give acetophenone.



Thus, [B] is acetophenone.

Since [A] on reaction with dil. H_2SO_4 and $HgSO_4$ is giving acetophenone, [A] must be having a C ≡ C bond and benzene ring. The possible structure of [A] is





[A] [B]

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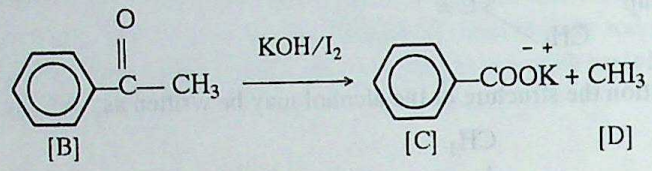
[B] is a methyl ketone. Thus on reaction with KOH and I_2 would undergo iodoform reaction to form yellow ppt. of iodoform and potassium salt of benzoic acid.



Thus, [C] is potassium benzoate and [D] is iodoform.

EXERCISE

VERY SHORT ANSWER QUESTIONS

ALKYL HALIDE ; ARYL HALIDES

1. Give IUPAC and trivial name of $C_6H_6Cl_6$.
2. Give common names of (*i*) $CH_2 = CH—CH_2Cl$ (*ii*) $(CH_3)_2CH—CH_2Cl$.
3. Give one chemical test is distinguish between C_2H_5Br and C_6H_5Br.
4. The thionyl chloride method is a better method of preparing alcohols, why ?
5. Write structural formula of 4-chloro-2-pentene.
6. Write the structures of isomers of formula $C_3H_6Cl_2$ and name them.
7. What are DDT and BHC ? Give one use for each.
8. What is freon ? Give one use.
9. What is pyrene ? Give one method of preparation.
10. Why allyl chloride is highly reactive towards reactions ?
11. Chorobenzene is inert towards chemical reaction ; why ?
12. Name the kind of isomerism shown by ethylene chloride and ethylidene dichloride.
13. How will you prepare *n*-propyl iodide from *n*-propyl bromide ?
14. What happens when sod. acetylide is treated with ethyl iodide ?
15. The m.p. of *p*-dichlorobenzene is greater than *o*-dichlorobenzene, why ?
16. What is Balz-schiemann reaction ?
17. How is 2-Butyne obtained from methyl iodide ?
18. Arrange all isomers of compound with formula C_4H_9Cl in increasing order of reactivity.
19. Which of the following is more reactive towards SN_2 type of reaction ?
    CH_3Br, $(CH_3)_2CHBr$, $(CH_3)_3CBr$.
20. Which alkyl halide has the highest density and why ?
21. Why chloroform is stored in dark bottles ?
22. Pyrene can be used in fire extinguisher, why ?
23. Chloroform administered to patients in surgical operations is tested with silver nitrate before administration.
24. The chlorine atom in chlorobenzene is ortho and para-directing.
25. What is Sandmeyer's reaction ?

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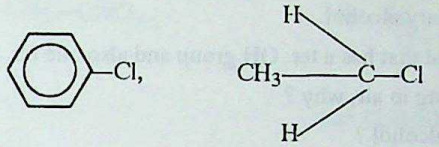
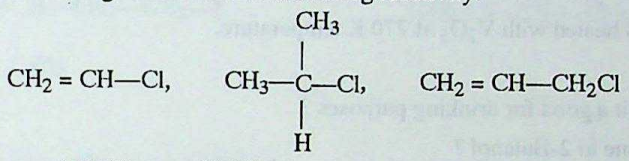
26. How will you distinguish two isomers of compound $C_2H_4Cl_2$?
27. Compare the bond length of C—Cl bond in chlorobenzene and ethylchloride.
28. Which of the two C—Cl bonds shown below will have more dipole moment.



29. Arrange the following in the order of increasing reactivity.



30. Give structures of (*i*) Westron (*ii*) Westrosol.
31. Why chlorobenzene cannot be hydrolysed with aq. NaOH at room conditions ?
32. What is Wurtz reaction ? What kind of alkyl halides give Wurtz reaction ?
33. What is chloropicrin and how do you obtain it.
34. Name the gas evolved when silver dust is heated with chloroform.
35. What is Finkelstein reaction ?
36. Alkyl halides do not produce a white ppt. with aq. $AgNO_3$, why ?
37. Alkanes cannot be easily converted to fluorides, why ?
38. What is the function of anhydrous $AlCl_3$ in chlorination of benzene ?
39. Why benzyl chloride is more reactive than chloro benzene ?
40. CCl_4 does not dissolve in water, why ?

ALCOHOLS AND PHENOLS

1. What are alcohols ?
2. Give classification of alcohols.
3. What is amyl alcohol ? Give its IUPAC name.
4. Give a chemical test to distinguish between 3° and 1° alcohols.
5. Phenol is acidic in character, why ?
6. Compare the dissociation constant of phenol with alcohol.
7. Phenol do not decompose sodium bicarbonate solution, why ?
8. Why phenol changes the colour of litmus ?
9. What happens when diazotised solution of aniline is treated with aq. KOH ?
10. Alcohols readily dissolve in water.
11. What is cumene ? How shall you convert it to phenol ?
12. Phenol change the colour litmus but alcohols do not.
13. Alcohols are insoluble in aq. NaOH but phenol is soluble, why ?
14. What is rectified spirit ?
15. How is absolute alcohol obtained ?
16. Give the correct order of reactivity of different alcohols towards esterification.
17. Name the products formed when branched isomers of C_4H_9OH are treated with conc. H_2SO_4 at 433 K.

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18. Name the product obtained when ter-butyl alcohol is heated with conc. H_2SO_4 and $K_2Cr_2O_7$?
19. What type of reactions do you expect to occur in alcohols ?
20. Arrange the alcohols in the order of increasing reactivity towards reaction with HCl in the presence of anhy $ZnCl_2$.
21. Name a primary, a secondary and a tertiary alcohol.
22. Write structure and IUPAC of an alcohol that has a ter. OH group and also one ter. H atom.
23. The colour of phenol changes on standing in air, why ?
24. Why is it not possible to prepare vinyl alcohol ?
25. What is allyl alcohol and how do you obtain it from acrolein ?
26. What happens when benzene is heated with V_2O_5 at 770 K temperature.
27. What is power alcohol ?
28. What is denatured alcohol ? Is it a good for drinking purposes ?
29. How can you change 2-Butanone to 2-Butanol ?
30. Covert 2-propanone to ter-butyl alcohol.
31. What are Glycerides ? Name one.
32. Glycerol is highly viscous in nature, why ?
33. Are the two —OH groups of glycol equally reactive ? Explain.
34. What is the structure of dioxane and name the compound from which you obtain it ?
35. What are cyanogens and how are these converted to glycol ?
36. Name an antipyretic and give its structure.
37. What is salol ? How do you obtain it ?
38. What is Reimer-Tiemann reaction ? What products can be obtained in this reaction ?
39. What is Glyceric acid ? How do you obtain it ?
40. Name the different type of OH groups present in Glycerol. Are they equally reactive ?
41. What happens when diazotised solution of aniline is treated with phenol ? Write equation only.
42. Arrange in order of increasing reactivity towards reaction with NaOH. *o*-nitrophenol, 2, 4-dinitro phenol, 2, 4, 6-trinitro phenol.
43. Why oxidation of phenol gives different products as compared to that of alcohols ?
44. The —OH group in phenol is ortho and para directing in nature.
45. Which out of 1°, 2° and 3° alcohol is more acidic in character ?

DESCRIPTIVE QUESTIONS

ALKYL AND ARYL HALIDES

Nomenclature and Isomerism

1. Give IUPAC names of the following :
   (*i*) *tert*-Butyl bromide (*ii*) *neo*-Pentyl chloride
   (*iii*) Allyl bromide (*iv*) Vinyl chloride.
2. How many isomeric aromatic compounds are possible for the molecular formula $C_6H_4Cl_2$. Give their structures and IUPAC names.
3. Write all the possible structures for the molecular formula $C_5H_{11}Br$. Give their IUPAC names and indicate which of them can exhibit enantiomerism.

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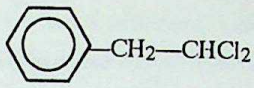
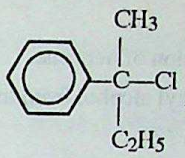
4. Give IUPAC names of the following compounds :

(*i*) 

(*ii*) 

(*iii*) $(C_2H_5)_3CBr$

(*iv*) $C_6H_5CH_2CH_2CH_2Br$

(*v*) $BrCH_2—CH_2Br$

(*vi*) $(CH_3)_3C—CHCl—CH_3$

(*vii*) $CH_3—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—CH_2—CH_2—I$

(*viii*) $Cl—CH_2—CH_2—CH_2—CH_2—Br$

(*ix*) $CH_2 = CH—\underset{\displaystyle C_2H_5}{\underset{|}{CH}}—\underset{\displaystyle Cl}{\underset{|}{C}} = CH_2$

(*x*) $Cl—CH_2—\overset{\displaystyle Br}{\overset{|}{C}} = \overset{\displaystyle Br}{\overset{|}{C}}—CH_2—Cl$

(*xi*) $ClCH_2—CH_2—\underset{\displaystyle CH_2Cl}{\underset{|}{CH}}—CH_2—CH_2Br$

(*xii*) $CH_2 = CH—\underset{\displaystyle Br}{\underset{|}{C}} = CH—CH = CH_2$

(*xiii*) $CH_3—CH_2—\overset{\displaystyle CH_3}{\overset{|}{\underset{\displaystyle Br}{\underset{|}{C}}}}—\underset{\displaystyle Br}{\underset{|}{CH}}—CH_2—Cl$ **[CBSE (O) 1994]**

5. How many isomeric aromatic compounds are possible for the molecular formula C_7H_7Br ? Give their IUPAC names.
6. Give common as well as IUPAC names of the two isomers having molecular formula $C_2H_4Cl_2$.
7. How many dichloro derivatives are possible for propane ? Give their structures and IUPAC names. Does any of them exhibit enantiomerism ?
8. Write structural formula of the following :
   (*i*) Benzal chloride (*ii*) 4-Chloro-2-pentene (*iii*) *Iso*-propylidene dichloride
   (*iv*) 1-Bromo-2, 2-dimethyl propane (*v*) 3-Chloro-2, 4-dimethylpentane

Methods of Preparation

9. How would you prepare *iso*-propyl bromide from each of the following ?
   (*i*) Propene (*ii*) 2-Propanol
   Give equations for the reactions.
10. How would you synthesize 1-bromobutane from 1-butene in single step ?
11. Write short note on Markownikoff's rule. Illustrate by taking at least two examples.
12. What is Kharasch effect ?
13. What happens when chlorine is passed through boiling toluene in the presence of sunlight ?
14. Explain why thionyl chloride is considered the best reagent for converting alcohols to alkyl chlorides.
15. How would you prepare allyl chloride from propene ?
16. Write short note on Sandmeyer's reaction.
17. Suggest a method for the preparation of aryl fluorides.

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18. How would you prepare the following compounds from 2-methyl propene ?

(*i*) *tert*-Butyl bromide (*ii*) *iso*-Butyl bromide.

19. Give mechanism of chlorination of benzene.

20. How would you prepare benzyl alcohol from toluene ?

21. What is Gattermann reaction ?

22. Starting from different reactants suggest two methods of preparation of *sec*-butyl chloride.

Physical and Chemical Properties

23. Explain why :

(*i*) 1-Chlorobutane has higher b.p. than 2-chlorobutane.

(*ii*) *p*-Dichlorobenzene has higher m.p. than *o*-dichlorobenzene.

(*iii*) Alkylhalides undergo nucleophilic substitution reactions.

(*iv*) Bromoethane has higher boiling point than chloroethane.

24. Alkyl halides are insoluble in water though they contain a polar C—X bond. Explain. ***(PSEB 1993)***

25. Out of methyl chloride and ethyl chloride which has higher boiling point and why ?

26. Out of ethyl chloride and ethyl bromide which has higher boiling point and why ?

27. How will you prepare the following from 2-*chlorobutane* :

(*i*) *sec*-Butyl ethyl ether (*ii*) 2-Butanol (*iii*) 2-Butane

(*iv*) *n*-Butane (*v*) 2-Aminobutane (*vi*) 2-Nitrobutane

(*vii*) 3, 4-Dimethylhexane.

28. Out of *chlorobenzene* and *ethyl chloride* which is more reactive and why ?

29. Giving suitable reason, arrange the following in decreasing order of reactivity.

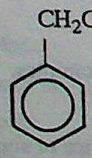
R—Cl, R—Br, R—I

30. Why are haloarenes more stable than haloalkanes and undergo electrophilic substitution at ortho and para positions ? ***[A.I. CBSE (O) 1991]***

31. Complete the following sequences of reactions by supplying A, B and C :

(*i*) $CH_3CH_2CH_2Br \xrightarrow[\Delta]{\text{alc. KOH}} (A) \xrightarrow{HBr} (B) \xrightarrow{\text{aq. KOH}} (C)$

(*ii*) $(A) \xrightarrow[Py]{SOCl_2} (B)$, $(B) \xrightarrow{Na/Ether} (C)$, $(B) \xrightarrow{NaOCH_3}$ 2-Methoxypropane

(*iii*) (A) 

$\xrightarrow[363\ K]{Cl_2}$ (A) $\xrightarrow[Warm]{\text{aq. KOH}}$ (B) $\xrightarrow{Cu/575\ K}$ (C)

32. Write short note on Williamson synthesis of ethers.

33. How would you convert methyl bromide into

(*i*) Ethanoic acid (*ii*) Ethyl amine

(*iii*) Ethanamide (*iv*) Methyl amine.

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34. (*a*) Write a chemical reaction to illustrate Saytzeff's rule. ***(H.P. Board 1994)***

(*b*) How would you prepare 2-pentyne from propyne ?

35. Among the various isomers of C_4H_9Br which would undergo elimination most readily and why ?

36. How would you convert benzene into

(*i*) *m*-chloronitrobenzene (*ii*) *p*-chloronitrobenzene.

37. How would you convert benzene into

(*i*) *m*-chlorobenzoic acid (*ii*) *p*-chlorobenzoic acid

38. Give the structures and names of the chief organic products expected from the reaction of *n*-butyl bromide with each of the following reagents :

(*i*) Zn/H^+ (*ii*) NaI/acetone

(*iii*) Mg/ether (*iv*) Li followed by CuI and ethyl bromide.

39. Why ring substitution in chlorobenzene occurs preferably at ortho and para position ?

40. Complete the following reactions giving equations :

(*i*) *sec*-Butyl iodide $\xrightarrow{\text{KOH (alc.)}}$ (*ii*) Chlorobenzene $\xrightarrow[\text{(ii) } H_2O/H^+]{\text{(i) CuCN/Py}}$

(*iii*) + $CH_3CH_2CH_2Cl$ $\xrightarrow[AlCl_3]{\text{Anhydrous}}$ ***(I.I.T. 1992)***

41. Give the structures of the compounds, *o-chloronitrobenzene* and *1-chloro-2-nitro-4-(trifluoromethyl) benzene.* One of the two has been found to react sodium methoxide involving replacement of —Cl group by —OCH_3 group, about 800 times faster than the other. Which one is more reactive ?

42. A halide with formula $C_6H_{13}I$ is found to give to isomeric alkenes 2-*methyl-2-pentene* and *4-methyl-2-pentene* on dehydrohalogenation with alcoholic KOH. Suggest its structure.

43. An organic compound (A) having molecular formula C_3H_7Cl on reaction with alcoholic solution of KCN gives compound (B). The compound (B) on hydrolysis with dilute HCl gives compound (C) and on reduction with H_2/Ni gives *1-aminobutane*, identify A, B, C.

44. How will you distinguish between

(*i*) Chlorobenzene and cyclohexyl chloride (*ii*) Chlorobenzene and benzylchloride

(*iii*) Vinylchloride and ethylchloride (*iv*) Alkylbromide and vinyl bromide.

(*v*) Chlorobenzene and bromobenzene.

45. Describe giving equations the following reactions :

(*i*) Wurtz-Fittig reaction (*ii*) Sandmeyer reaction

(*iii*) Finkelstein reaction (*iv*) Hunsdiecker reaction.

Polyhalogen Compounds

46. Describe the preparation of chloroform from ethanol using bleaching powder.

47. Give the reaction of *chloroform* with

(*i*) Zn/HCl (*ii*) air in the presence of sun light

(*iii*) aniline in the presence of alcoholic KOH (*iv*) acetone.

48. Give the preparation of iodoform. What is iodoform test ?

49. How is iodoform prepared from acetone ? Give the reactions taking place.

50. What precautions are usually taken while storing chloroform ?

51. What products are formed when chloroform is

(*i*) heated with silver powder (*ii*) boiled with aqueous KOH

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(*iii*) heated with phenol in the presence of alcoholic KOH at 340 K

(*iv*) Warmed with CH_3NH_2 and alcoholic KOH.

52. Account for the following :

(*i*) Chloroform is a chlorine compound but is does not give white precipitate with silver nitrate solution.

(*ii*) Iodoform is obtained by the reaction of acetone with hypodite but not iodide ion. *(IIT 1991)*

(*iii*) While storing chloroform a small amount of ethanol is added to it.

53. Give a method for the preparation of pure chloroform.

54. What is IUPAC name of DDT ? How is it prepared ?

55. How would you convert :

(*i*) CCl_4 to chloroform ? (*ii*) CCl_4 to freon ?

56. How is BHC prepared ? What is its IUPAC name ?

57. Complete the following reactions ?

(*i*) $CH_3COCH_3 \xrightarrow{I_2/NaOH}$ (*ii*) $CH_3COCH_3 \xrightarrow{\text{Bleaching powder}}$

(*iii*) $CH_3CH_2OH \xrightarrow{I_2/NaOH}$ (*iv*) $CHCl_3 + HNO_3 \xrightarrow{\text{Heat}}$

(*v*) $CHCl_3 + (CH_3)_2C=O \longrightarrow$

ALCOHOLS AND PHENOLS

Nomenclature and Isomerism

58. Give IUPAC names of the following :

(*i*) *iso*-Butyl alcohol (*ii*) Glycerol

(*iii*) Propargyl alcohol (*iv*) *tert*-Pentyl alcohol.

59. How many isomeric aromatic compounds are possible for the molecular formula C_7H_8O ? Give their structures and IUPAC names.

60. Give structures of the following alcohols and classify them into primary, secondary and tertiary alcohols.

(*i*) 2-Methyl-2-propanol (*ii*) 2-Propanol

(*iii*) 1-Butanol (*iv*) 3-Methyl-2-pentanol.

61. Give structures and IUPAC names of all the isomeric compounds having molecular formula C_3H_8O.

62. Name the following compounds according to IUPAC system :

(*i*) $CH_3-CH=C(OH)-CH(CH_3)-CH_2-CH_3$ (*ii*) $C_6H_5-CH(Cl)-CH_2-CH_2-CH_2OH$.

63. Give one example each of a monohydric, dihydric and trihydric phenol.

64. Give structures and IUPAC names of all the isomeric alcohols having molecular formula $C_4H_{10}O$. Which of them can exhibit enantiomerism ?

Properties of Alcohols and Phenols

65. How do you account for the fact that unlike phenol, 2, 4-dinitrophenol and 2, 4, 6-trinitrophenol are soluble in aqueous solution of sodium carbonate ?

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66. Account for the following :

(*i*) Alcohols are generally soluble in water but alkyl halides are not.

(*ii*) Boiling points of alcohols are higher than that of corresponding alkanes.

(*iii*) Boiling points of alcohols are higher than that of haloalkanes of comparable molecular mass.

(*iv*) Dipole moment of methanol is higher than that of phenol.

67. Arrange the following in increasing order of their boiling points :

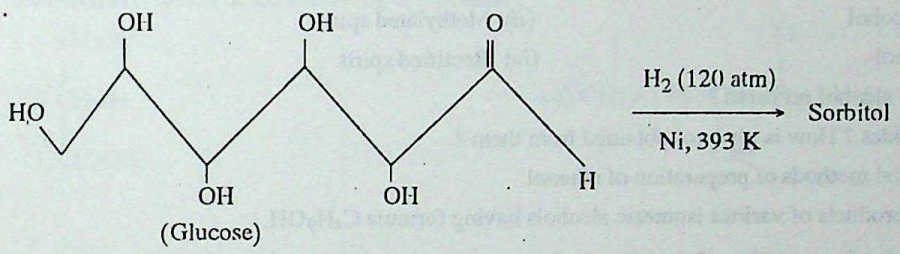
(*i*) $CH_3CH_2CH_2CH_2OH$ (*ii*) $CH_3CH_2CH_2Cl$

(*iii*) $CH_3CH_2CH_2CH_2CH_3$ (*iv*) $(CH_3)_3C—OH$.

68. What are primary, secondary and tertiary alcohols ? How you will distinguish between them ?

[*A.I. CBSE (O) 1992*]

69. Sorbitol, which is commonly given to diabetics in place of cane sugar is prepared as shown below. Suggest its structure



70. (*a*) Why are phenols more acidic than alcohols ? **(*Pb. P.M.T. 1991 ; H.P. Board 1993*)**

(*b*) Give one test to distinguish between methanol and ethanol.

(*c*) Alcohols are generally soluble in water **(*P.S.E.B. 1993*)**

71. How will you prepare ethyl alcohol from

(*i*) Ethylene (*ii*) Acetaldehyde.

72. Discuss the dehydration of alcohol under different conditions.

73. What are monohydric alcohols ? How have they been classified ?

74. Account for the following :

(*i*) Boiling point of the C_2H_5OH is more than that of C_2H_5Cl.

(*ii*) The solubility of alcohols in water decreases with increase in molecular mass.

75. Arrange the following alcohols in order of increasing reactivity towards esterification reaction

(*i*) CH_3CH_2OH (*ii*) $(CH_3)_2CHOH$ (*iii*) $(CH_3)_3COH$.

76. (*i*) What is the order of reactivity of 1°, 2° and 3° alcohols with sodium metal ?

(*ii*) How will you account for the solubility of lower alcohols in water ?

77. How is phenol obtained from the following :

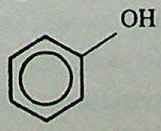
(*i*) Benzene diazonium chloride (*ii*) Sodium benzene sulphonate

(*iii*) Cumene (*iv*) Phenyl magnesium bromide.

78. What is Lucas reagent ? How does it help in distinguishing the primary, secondary and tertiary alcohols ?

79. Explain, why phenol slowly acquires pink colour on long standing.

80. How will you distinguish between the following pairs by chemical compounds ?

(*i*) C_2H_5OH and 

(*ii*) CH_3OH and C_2H_5OH (*iii*) 1-Propanol and 2-Propanol.

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81. Write short notes on :

(*i*) Reimer Tiemann reaction (*P.S.E.B. 1992*)

(*ii*) Kolbe reaction (*H.P. Board 1992*)

(*iii*) Coupling reaction. (*H.P. Board 1992*)

82. Sodium metal may be used to remove last traces of water from benzene but not from ethanol. Explain why.

83. Account for the following :

(*i*) Phenols are acidic in nature

(*ii*) *o*-Nitrophenol is steam volatile where as *p*-nitrophenol is not.

(*iii*) Phenols undergo substitution at *ortho* and *para* positions.

Some Common Alcohols

84. What is meant by :

(*i*) Absolute alcohol (*ii*) Methylated spirit

(*iii*) Power alcohol (*iv*) Rectified spirit.

How is absolute alcohol prepared ?

85. What are glycerides ? How is glycerol obtained from them ?

86. Give the industrial methods of preparation of ethanol.

87. Give oxidation products of various isomeric alcohols having formula C_4H_9OH.

88. Give two methods of preparation of glycol.

89. Describe giving chemical equations the reaction between :

(*i*) Glycerol and potassium bisulphate (*P.S.E.B. 1993*)

(*ii*) Glycerol and HI (*iii*) Ethylene glycol and HIO_4.

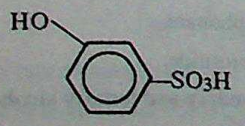
SOME MISCELLANEOUS QUESTIONS

90. An organic compound (A) with formula $C_4H_{10}O$ is optically active. On mild oxidation it gives compound (B) (C_4H_8O) and upon vigorous oxidation (A) gives another compound (C) $C_2H_4O_2$. B also gives (D) on treatment with I_2 in the presence of alkali. Deduce the structures of A, B, C and D.

91. Complete the following sequences of reactions by supplying X, Y and Z :

(*i*) $(X) \xrightarrow{LAH} (Y) \xrightarrow{PBr_3} (Z) \xrightarrow{Na/ether}$ 2, 3-Dimethyl butane

(*ii*) $(X) \xrightarrow[300\ atm]{NaOH,\ 575\ K} (Y) \xrightarrow{Conc.\ HNO_3}$ Picric acid

(*iii*) 

$\xrightarrow[(ii)\ Fuse]{(i)\ NaOH} (X)$

(*iv*) $(CH_3)_2CCl\,CH_2CH_3 \xrightarrow{KOH\ (alc.)} (X)$

(*I.I.T. 1992*)

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92. Give IUPAC names of the following compounds :

(*i*) $CH_3—\underset{\underset{C_2H_5}{|}}{CH}—CH_2Cl$ (*ii*) $\begin{array}{c} CH_2OH \\ | \\ CH_2 \\ | \\ CH_2OH \end{array}$ **(*C.B.S.E. 1992*)**

93. How are the following conversions carried out ? (Give equations)

(*i*) Aniline into fluorobenzene (*ii*) Ethene into ethanediol. **(*C.B.S.E. 1993*)**

94. Complete the following reaction equations :

(*i*) $CH_3CH_2NH_2 + CHCl_3 \xrightarrow{KOH}$ (*ii*) $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow$ **(*C.B.S.E. 1993*)**

95. State IUPAC names of the following compounds :

(*i*) $\begin{array}{c} CH_2OH \\ | \\ CHOH \\ | \\ CH_2OH \end{array}$ (*ii*) $CH_2 = CH—\underset{\underset{\underset{\underset{CH_3}{|}}{CH_2}}{|}}{CH}—\overset{\overset{Cl}{|}}{C} = CH_2$ **(*A.I. CBSE 1993*)**

96. Bring about the following conversions :

(*i*) Ethyl alcohol into diethyl ether (*ii*) Acetone to tert-butyl alcohol **(*A.I. CBSE 1993*)**

97. *n*-Butane is produced by monobromination of ethane followed by Wurtz reaction. What volume of ethane at N.T.P. is required to produce 58 g of *n*-butane if bromination occurs with 90% yield and Wurtz reaction occurs with 85% yield. **(*I.I.T. 1989*)**

98. Starting with phenol how will you get

(*i*) Cyclohexanol (*ii*) 1, 3, 5-Tribromobenzene

(*iii*) 2-Acetoxy benzoic acid.

99. The resonating structures of vinyl chloride are given below :

$$CH_2 = CH—\ddot{\underset{\cdot\cdot}{Cl}}: \longleftrightarrow : \overset{-}{C}H_2—CH = \overset{+}{\underset{\cdot\cdot}{Cl}}:$$

(*i*) Draw the probable hybrid structure.

(*ii*) What conclusion do you get about the reactivity of vinyl chloride towards nucleophilic substitution reaction as compared to C_6H_5Cl.

100. An aromatic compound A (C_6H_6O) produces compound (B) on treatment with CCl_4/NaOH and subsequent hydrolysis. B on zinc dust treatment gives monocarboxylic acid C. Sodium salt of C on soda lime decarboxylation gave an aromatic hydrocarbon D. A also gives purple colour with $FeCl_3$ solution. Suggest the structures of A, B, C and D.

101. Draw the resonating structures of phenol and predict whether —OH group is meta directing or *o*- and *p*-directing towards ring substitution reactions.

102. K_a of phenol and *p*-hydroxy benzaldehyde are found to be 1×10^{-10} and 2.4×10^{-8} respectively. How do you account for this ?

103. Give reasons :

(*i*) Chloroform is a chlorine compound but it does not give white precipitate with silver nitrate solution.

(*ii*) Nitration of phenol gives ortho- and para- products only.

(*iii*) Why do alcohols have higher boiling points than the haloalkanes of the same molecular weight.

(*H.P. Board 1993*)

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104. Give equations for the reaction of :

(*i*) Ethylene glycol and periodic acid (*ii*) Ethylene glycol and acidic $KMnO_4$

(*iii*) Glycerol and excess of HI *(P.S.E.B. 1993)*

(*iv*) Glycerol and fenton's reagent. *(P.S.E.B. 1993)*

105. What is Williamson's synthesis ? What type of compounds are prepared by this reaction ? Give an example. *[C.B.S.E. (O) 1994 (1)]*

106. Of benzene and phenol which is more easily nitrated and why ? *[C.B.S.E. (O) 1994 (1)]*

107. Explain the mechanism of the following reaction :

$$2C_2H_5OH \xrightarrow[413\ K]{conc.\ H_2SO_4} C_2H_5—O—C_2H_5 + H_2O.$$ *[C.B.S.E. (O) 1994 (1)]*

108. Give a chemical test to distinguish between :

(*i*) Ethanol and 1-propanol (*ii*) Chlorobenzene and benzyl chloride. *(C.B.S.E. 1995)*

109. How can diethyl ether be prepared from :

(*a*) Ethyl iodide (*b*) Ethyl alcohol. *(P.S.E.B. 1995)*

110. How is phenol prepared from :

(*i*) Benzene (*ii*) Chlorobenzene

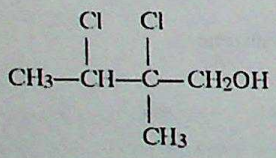
(*iii*) Benzene diazonium chloride. *(P.S.E.B. 1995)*

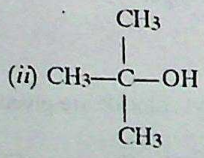
111. How will you convert glycerol into

(*i*) Allyl alcohol (*ii*) Acrolein (*iii*) Isopropyl iodide. *(P.S.E.B. 1995)*

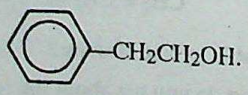
112. Write the synthesis is of glycerol starting from its elements. *(Haryana Board 1995)*

113. Write IUPAC names of the following compounds :

(*i*) 

(*ii*) 

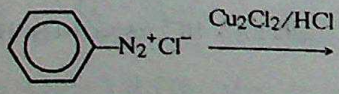
(*iii*) $HO—CH_2—CH_2—OH$

(*iv*)  *(Haryana Board 1995)*

COMPLETING THE EQUATIONS

Complete the following equations :

1. $CH_3CH = CH_2 + HBr \xrightarrow{Peroxide}$

2. 

3. $C_6H_5Cl \xrightarrow{Na/ether}$

4. $C_6H_6 + (CH_3)_2CHCH_2Cl \xrightarrow{AlCl_3}$

5. $C_2H_5Br + C_2H_5ONa \longrightarrow$ *(I.I.T. 1992)*

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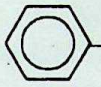
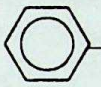
6. $C_6H_5CH_2CH(Br)CH_3 \xrightarrow{\text{alc. KOH}} ? \xrightarrow{\text{HBr}} ?$ *(I.I.T. 1993)*

7.  —ONa + CO_2 $\xrightarrow{\text{400 K, 4–7 atm}}$ *(H.P. Board 1991)*

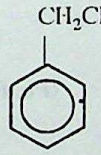
8.  —OH + Br_2 $\xrightarrow{H_2O}$

9. $C_2H_5OH + CH_3MgI \longrightarrow$

10. $C_6H_5OH + PCl_5 \longrightarrow$ *(H.P. Board 1991)*

11. $(CH_3)_2C(Cl)—CH_2CH_3 \xrightarrow{\text{alc. KOH}}$

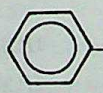
12. + $(CH_3)_2CHCl$ $\xrightarrow{AlCl_3}$

13. 

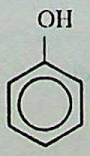
$\xrightarrow[\text{(ii) aq. KOH}]{\text{(i) } Cl_2\text{, Heat Light}}$

14. $CH_3—C(CH_3)(OH)—CH—CH_3 \xrightarrow{\text{conc. } H_2SO_4}$

15. $CH_3—C(Cl)(Cl)—CH_3 \xrightarrow[\text{alkali}]{\text{Boil}}$

16.  —CH_3 $\xrightarrow{Br_2\text{, Reflux, Light}}$? $\xrightarrow{\text{aq. KOH}}$?

17. $CH_2 = CH_2 \xrightarrow{Cl_2, H_2O} ? \xrightarrow{Na_2CO_3, H_2O} ?$

18. 

$\xrightarrow[\text{CCl}_4\text{, 340 K}]{\text{aq. KOH}} ? \xrightarrow{H^+} ? \xrightarrow[H_2SO_4]{(CH_3CO)_2O} ?$

Complete the following sequences of reactions by supplying X, Y and Z :

19. $X \xrightarrow{\text{HBr}} CH_3—CH(Br)—CH_3 \xrightarrow{\text{alc. KOH}} Y \xrightarrow[\text{peroxide}]{\text{HBr}} Z$

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20. $CH_3Br \xrightarrow{KCN} X \xrightarrow{Conc.\ HCl} Y$

21.
$\xrightarrow{Cl_2/FeCl_3} X \xrightarrow[Py]{CuCN} Y \xrightarrow{dil.\ HCl} Z$

22. $CH_3CH_3 \xrightarrow[Heat]{Cl_2} X \xrightarrow[AlCl_3]{C_6H_6} Y \xrightarrow[Heat,\ light]{Cl_2} Z$

23. $X \xrightarrow{PBr_3} Y \xrightarrow[ether]{Na} CH_3CH_3 \xrightarrow[Heat]{Cl_2} Z$

24. $X \xrightarrow{H_2O/H^+} CH_3\underset{\underset{OH}{|}}{C}HCH_3 \xrightarrow{Cu/575\ K} Y \xrightarrow[(ii)\ H_2O/H^+]{(i)\ C_2H_5MgI} Z$

WHAT HAPPENS WHEN

State giving equations as to what happens when :

1. Chloroform is warmed with ethylamine and alcoholic KOH.
2. 2-Methyl-2-propanol is passed over heated copper. *(Pb. P.M.T. 1990)*
3. Chloroform is boiled with KOH solution.
4. Phenol is distilled with phthalic anhydride in the presence of H_2SO_4.
5. Glycerol is allowed to react with nitric acid.
6. A piece of sodium metal is put into isopropyl alcohol.
7. A few drops of neutral $FeCl_3(aq)$ are added to phenol.
8. Ethyl chloride dissolved in acetone is treated with sodium iodide.
9. Glycerol is oxidised with Fenton's reagent.
10. Phenol is refluxed with conc. H_2SO_4 at 373 K.
11. 2, 4, 6-Trinitrophenol is heated with zinc dust.
12. Silver propionate is refluxed with bromine in CCl_4.
13. Benzene diazonium chloride is warmed with KI. *(P.S.E.B. 1983)*
14. Benzenediazonium chloride is treated with alkaline ice cold phenol. *(P.S.E.B. 1993)*
15. Phenol is treated with Br_2 in the presence of CS_2 as solvent at 273 K.
16. Chlorobenzene is treated with sodium in the presence of ether as solvent.
17. Ethanol is added to the ethereal solution of *iso*-propyl magnesium iodide.
18. Ethyl acetate is treated with excess MeMgI and the product is hydrolysed in the presence of acid.
19. Ethylene glycol is heated with anhydrous zinc chloride.
20. Glycerol is treated with sodium at room temperature.
21. Iodoform is warmed with primary amine and alcoholic KOH. *(H.P. Board 1992)*
22. Chloroform is heated with a solution of phenol in sodium hydroxide. *(Haryana Board 1994)*
23. Chloroform is exposed to sunlight and air for a long time. *(C.B.S.E. 1995)*
24. Phenol is warmed with CCl_4 in the presence of aqueous NaOH. *(C.B.S.E. 1995)*

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CONVERSIONS

How will you bring about the following conversions :

1. Ethyl alcohol to ethylene glycol. *(CBSE 1992)*
2. Ethyl bromide to propyl amine.
3. Ethyl bromide to propionic acid.
4. Toluene to benzyl chloride.
5. Benzene to *o*-nitro chlorobenzene.
6. Ethyl bromide to *n*-butane.
7. *n*-Propyl bromide to isopropyl bromide.
8. 2-Propanol to 1-Bromopropane. *(CBSE 1992)*
9. Benzene to *p*-chlorobromobenzene.
10. Benzene to *m*-chlorobromobenzene.
11. Acetone to 2-methyl-2-propanol. *(CBSE 1990)*
12. Benzene to phenol.
13. Propylene to glycerol.
14. Ethylene to *n*-propyl alcohol. *(CBSE 1990)*
15. 1-Butene to 1-Butanol.
16. Ethyne to iodoform.
17. Propene to 2, 3-Dimethyl butane.
18. Chlorobenzene to Benzene. *(Pb. P.M.T. 1990)*
19. Glycerol to acrolein
20. Ethylene glycol to dioxane
21. Ethanol to Methanol. *(CBSE 1992)*
22. Chloroform to Diethyl carbonate. *(CBSE 1992)*
23. Ethylamine to Ethyl isocyanide. *(P.S.E.B. 1983)*
24. Benzene to 1-phenylethanol.
25. Benzene to styrene.
26. Benzene to 2-phenylethanol.
27. Chloroform to acetylene. *(P.S.E.B. 1994)*
28. Chlorobenzene to aniline. *(P.S.E.B. 1994)*
29. Chlorobenzene to toluene. *(H.P. Board 1994)*
30. Ethanol to 1, 2-ethanediol. *(C.B.S.E. 1994)*
31. Propanone to iodoform. *(C.B.S.E. 1994)*
32. Ethanol to 2-propanol. *(C.B.S.E. 1994)*

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select the correct answers

1. Which of the following represents a *Gem* dihalide ?
   (*a*) Ethylene dichloride (*b*) 2, 2-dichloropropane
   (*c*) 1, 3-dichloropropane (*d*) 1, 2-dichloropropane.
2. Pure chloroform is obtained by treating
   (*a*) Ethanol with bleaching powder (*b*) Acetone with bleaching powder
   (*c*) Chloral with NaOH (*d*) CCl_4 with moist iron.
3. Chloroform on heating with aniline and alcoholic KOH gives
   (*a*) Phenyl cyanide (*b*) Phenyl isocyanide (*c*) *p*-Chloro aniline (*d*) Chloroamine.
4. $X \xrightarrow[(ii)\ AgNO_3(aq)]{(i)\ KOH(aq)}$ white ppt. In this reaction X can be
   (*a*) Chlorobenzene (*b*) Vinyl chloride (*c*) Ethanol (*d*) *Iso*-Propyl chloride.
5. Alcoholic solution of KOH is a specific reagent for
   (*a*) Dehydration (*b*) Dehalogenation (*c*) Dehydrohalogenation (*d*) Dehydrogenation.
6. Best reagent for preparing a chloroalkane from an alcohol is
   (*a*) $SOCl_2/C_5H_5N$ (*b*) $HCl/ZnCl_2$ (*c*) PCl_3 (*d*) Cl_2/CCl_4.
7. Ethanol on heating with conc. H_2SO_4 at 445 K gives
   (*a*) Diethyl sulphate (*b*) Ethylene, C_2H_4
   (*c*) Diethyl ether, $(C_2H_5)_2O$ (*d*) Ethyl hydrogen sulphate, $C_2H_5HSO_4$.
8. Which of the following is most acidic ?
   (*a*) H_2O (*b*) CH_3OH (*c*) C_2H_5OH (*d*) $CH_3CH_2CH_2OH$.
9. Which of the following has highest boiling point ?
   (*a*) $CH_3CH_2CH_2OH$ (*b*) $CH_3CH_2CH_2CH_2OH$
   (*c*) $(CH_3)_2CH—CH_2OH$ (*d*) $CH_3—C(CH_3)_2—OH$
10. $C_6H_5Cl \xrightarrow[623\ K,\ 300\ atm]{NaOH(aq)}$ A. Here, A is
    (*a*) Phenol (*b*) Sodium phenoxide
    (*c*) Benzene (*d*) Cyclohexyl chloride.
11. Which of the following represents freon ?
    (*a*) Ethylene dichloride (*b*) Ethylidene dichloride
    (*c*) Tetrafluoroethylene (*d*) Dichlorodifluoromethane.
12. Which of the following alcohols can be obtained from HCHO ?
    (*a*) CH_3OH (*b*) C_2H_5OH (*c*) $CH_3CH_2CH_2OH$ (*d*) All of these.

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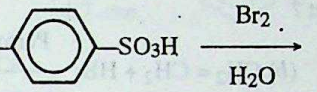
13. The most reactive among the given compounds is

(*a*) $CH_2 = CH—Cl$ (*b*) $CH_2 = CHCH_2Cl$ (*c*) CH_3CH_2Cl (*d*) C_6H_5Cl.

14. The order of reactivity among (*i*) Phenol (*ii*) *p*-nitrophenol (*iii*) 2, 4-Dinitro phenol follows as

(*a*) (*i*) = (*ii*) = (*iii*) (*b*) (*i*) < (*ii*) < (*iii*) (*c*) (*ii*) < (*ii*) = (*iv*) (*d*) (*i*) < (*iii*) < (*ii*).

15. In the sequence 

X, X is

(*a*) 2-Bromo-4-hydroxy benzene sulphonic acid (*b*) 3, 5-Dibromo-4-hydroxy benzene sulphonic acid

(*c*) 2-Bromophenol (*d*) 2, 4, 6-Tribromophenol.

16. Phenol can be distinguished from ethyl alcohol by all reagents except

(*a*) NaOH (*b*) $FeCl_3$ (*c*) Br_2/H_2O (*d*) Na.

17. On heating ethylene glycol at 775 K the product obtained is

(*a*) Oxirane (*b*) Acetaldehyde (*c*) Glycoaldehyde (*d*) Dioxane.

18. Alcohols can be obtained from all methods except

(*a*) Hydroboration-oxidation (*b*) Oxymercuration-demercuration

(*c*) Reduction of aldehyde/ketones with Zn—Hg/HCl (*d*) by fermentation of starch.

19. Which of the following compounds is least acidic ?

(*a*) *o*-Nitrophenol (*b*) *m*-Nitrophenol (*c*) *p*-Nitrophenol (*d*) Phenol.

20. Which one of the following is likely to give a precipitate with $AgNO_3$ solution ?

(*a*) CCl_4 (*b*) $CHCl_3$ (*c*) $CH_2 = CHCl$ (*d*) $(CH_3)_3CCl$.

21. Which of the following alcohols is least soluble in water ?

(*a*) *n*-Butyl alcohol (*b*) *iso*-Butyl alcohol (*c*) *tert*-Butyl alcohol (*d*) *sec*-Butyl alcohol.

22. Anti-Markownikoff addition of HBr is not observed in

(*a*) Propene (*b*) 1-Butene (*c*) 2-Butene (*d*) 2-Pentene.

23. Alkyl halides can be converted to alkenes by

(*a*) Substitution (*b*) Addition (*c*) Elimination (*d*) Rearrangement.

24. 1, 1-Dichloropropane on hydrolysis gives

(*a*) Propanone (*b*) Propanal (*c*) Ethanal (*d*) 1, 1-Propanediol.

25. The compound which is most acidic among the following is

(*a*) Phenol (*b*) *p*-Nitrophenol (*c*) *o*-Nitrophenol (*d*) *m*-Nitrophenol.

26. Which of the following alcohols would give positive iodoform test ?

(*a*) Ethanol (*b*) 1-Propanol (*c*) 2-Propanol (*d*) Methanol.

27. Which of the following compounds are isomeric with 1-propanol ?

(*a*) Ethanal (*b*) 2-Propanol (*c*) 1-Butanol (*d*) Ethylmethyl ether.

28. Which of the following compounds would give a ketone on oxidation ?

(*a*) *iso*-Butyl alcohol (*b*) *iso*-Propyl alcohol (*c*) *iso*-Pentyl alcohol (*d*) *sec*-Butyl alcohol.

29. Which of the following compounds would not give a precipitate with alcoholic solution of $AgNO_3$?

(*a*) Bromobenzene (*b*) 2-Bromopropane (*c*) Allyl bromide (*d*) 2-Bromopropene.

30. Which of the following is/are primary halides ?

(*a*) *iso*-Propyl chloride (*b*) *iso*-Butyl chloride (*c*) *neo*-Pentyl chloride (*d*) *sec*-Butyl bromide.

31. Which of the following would not react with aq. KOH easily ?

(*a*) 1-Chloropropene (*b*) 2-Chloropropene (*c*) 3-Chloropropene (*d*) 1-Chloropropane.

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32. Only two isomeric monochloro derivatives are possible for :

(*a*) *n*-Butane (*b*) Benzene (*c*) 2, 4-Dimethylpentane (*d*) 2-Methyl propane.

33. Which of the following would yield carboxylic acid as the product on oxidation with acidified $K_2Cr_2O_7$?

(*a*) 1-Butanol (*b*) 1-Propanol (*c*) 2-Propanol (*d*) 2-Butanol.

34. Which of the following would exhibit Kharasch effect ?

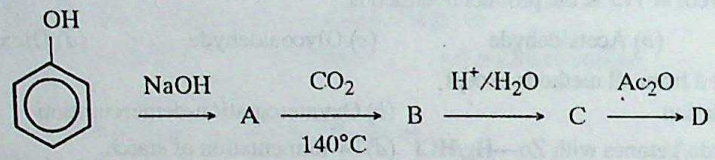
(*a*) $CH_3CH = CH_2 + HCl \xrightarrow{\text{Peroxides}}$ (*b*) $CH_2 = CH_2 + HBr \xrightarrow{\text{Peroxides}}$

(*c*) $CH_3CH = CH_2 + HBr \xrightarrow{\text{Peroxides}}$ (*d*) $CH_3CH = CHCH_2CH_3 + HBr \xrightarrow{\text{Peroxides}}$.

35. Which of the following reagents/conditions can convert 2-propanol to acetone ?

(*a*) $LiAlH_4$ (*b*) Cu/575 K (*c*) $K_2Cr_2O_7/H^+$ (*d*) H_2/Pd.

36. The end product of the following sequence of reactions is



(*a*) Salicyclic acid (*b*) Salicylaldehyde (*c*) Phenyl acetate (*d*) Aspirin.

37. The product obtained from the following sequence of reaction is

$$HC \equiv CH \xrightarrow[H_2SO_4]{HgSO_4} A \xrightarrow{LAH} B$$

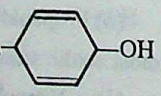
(*a*) Acetaldehyde (*b*) Ethanol (*c*) Glycol (*d*) Acetic acid.

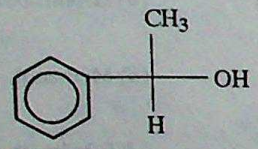
38. The starting material used in the following reaction is

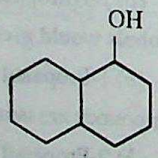
$$A \xrightarrow[160°]{H_2SO_4} B \xrightarrow[(ii)\ \text{aq KOH}]{(i)\ HBr} (CH_3)_3COH$$

(*a*) Propanol-2 (*b*) 2-Butanol (*c*) iso-butyl alcohol (*d*) iso-butylene.

39. An example of benzylic alcohol is

(*a*) $CH_3CH = CHCH_2OH$ (*b*) 

(*c*) 

(*d*) 

40. In the sequence of reactions, $C_6H_5MgBr \xrightarrow{(CH_2)_2O} A \xrightarrow{H_2O} B$

The product in the reaction is,

(*a*) Phenol (*b*) 2-Phenyl ethanol (*c*) Benzyl alcohol (*d*) Resorcinol.

FILL IN THE BLANKS

Complete the following equations/statements.

1. $CH_3CH_2OH + SOCl_2 \longrightarrow$

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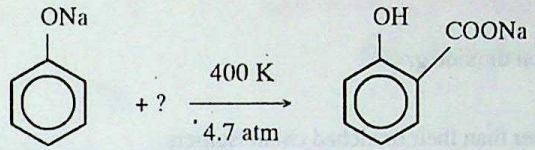
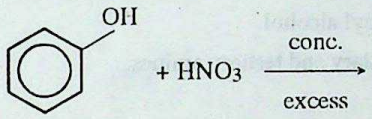
2. $RCH_2OH \xrightarrow{?} RCH_2Br \xrightarrow{?} RCH_2CN \xrightarrow{?} RCH_2COOH$ *(H.P. Board 1993)*

3. 

4. $CH_3CH_2OH \xrightarrow[573\ K]{Cu}$

5. 

6. Butane nitrile can be prepared by heating ..... with alcoholic KCN. *(I.I.T. 1992)*
7. Amongst three isomers of nitrophenol, the one that is least soluble in water is ..... *(I.I.T. 1992)*
8. The common name of 1, 2, 3-trihydroxybenzene is .....
9. IUPAC name of cumene is .....
10. Pyrene is a name given to .....
11. Ethyl bromide on reaction with moist silver oxide gives ..... as the main product.
12. Phenol reacts with sodium liberating ..... gas.
13. The reaction of phenol with benzoyl chloride in the presence of alkali is known as ..... reaction.
14. Among isomeric alkyl chlorides having molecular formula C_4H_9Cl, the one with the highest boiling point is .....
15. In S_N^1 mechanism, ... are involved as intermediate species.
16. IUPAC name of picric acid is .....
17. Phenol is ..... reactive than chlorobenzene towards electrophilic substitution reactions.
18. 2, 2-Dichloropropane on reaction with aq. KOH yields ..... as the main product.
19. In case of ..... alcohols, the cloudiness appears immediately while performing Lucas test.
20. During acid catalysed dehydration of alcohols, the intermediate species involved are .....

TRUE/FALSE STATEMENTS

State whether the following statements are true or false :

1. Phenyl chloromethane is an aryl halide.
2. *neo*-Pentyl chloride is a primary halide.
3. Ethylene dichloride is a geminal dihalide.
4. *Iso*-butyene on reaction with HBr gives *iso*-butyl bromide.
5. NBS is a specific reagent for allylic substitution in alkenes.
6. Aryl fluorides can be prepared by Sandmeyer reaction.
7. Methyl fluoride has higher boiling point than methyl chloride.
8. During dehydrohalogenation, the hydrogen atom is removed from the α-carbon.
9. Vinyl chloride is less reactive than allyl chloride towards nucleophilic substitution reactions.

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10. Cl atom attached to benzene ring directs the next electrophilic substitution towards *ortho* and *para* position, and deactivates the ring.
11. Phenols turn blue litmus red.
12. Phenols react with Na_2CO_3 and liberate carbon dioxide gas.
13. Alcohols are stronger acids than water.
14. Straight chain alcohols are less soluble in water than their branched chain isomers.
15. Methanol gives iodoform test.
16. Luca's reagent is equimolar mixture of HCl and zinc chloride.
17. Methylated alcohol is unfit for drinking.
18. Reactivity of methanol with sodium is more than that of Isopropyl alcohol.
19. Carbylamine test is used to distinguish between primary, secondary and tertiary amines.
20. 2-Butanol can exhibit enantiomerism.

MATCHING TYPE QUESTIONS

1. ***Match the following items :***

A. Aralkyl halide	1. CH_3CH_2OH/HCl-anhyd. $ZnCl_2$
B. Allyl chloride	2. $(CH_3)_2C(OH)CCl_3$
C. Sandmeyers reaction	3. Hexachloro cyclohexane
D. Westrosol	4. $C_6H_5NH_2 + CHCl_3 + KOH$
E. Groove's process	5. 3-Chloro-1-propene
F. Lindane	6. $CH_3COCH_2CH_3$
G. Chloretone	7. ter-butyl chloride
H. Carbyl amine reaction	8. $C_6H_5CH_2Cl$
I. Silver nitrate test	9. $CHCl = CCl_2$
J. Iodoform test	10. $C_6H_5N_2^+Cl^-/HCl—CuCl$

2. ***Match the following items :***

A. Fermentation	1. tertiary alcohol
B. Dyananute	2. Phenol
C. Enzyme	3. Mixture of petrol and ethyl alcohol
D. Lucas test	4. Ethyl alcohol
E. Coupling test	5. Nitro glycerine
F. Methylated spirit	6. 1, 2, 3-propane triol
G. Power alcohol	7. $CH_3COOC_2H_5$
H. Glycerine	8. 100% ethyl alcohol
I. Fischer-Speier reaction	9. Invertase
J. Absolute alcohol	10. Methyl alcohol.

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ANSWERS

REVIEW PROBLEMS

7.1. (*a*) $CH_3-\underset{\underset{Cl}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_3$ (2-chloro-2-methyl butane)

(*b*) $CH_3\underset{\underset{I}{|}}{C}HCH_2CH_3$ (2-Iodobutene)

(*c*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2Br$ (1-Bromo-4, 4-dimethyl pentane)

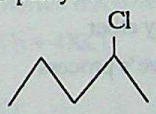
(*d*) $(CH_3)_2CH-CH_2CH_2Cl$ (1-chloro-3-methyl butane)

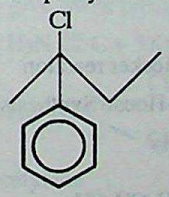
7.2. (*i*) $CH_3CH_2\overset{\overset{Br}{|}}{C}HCH_2CH_2CH_3$ (*ii*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_2CH_2I$ (*iii*) $\begin{array}{l}CH_2Br\\|\\CH_2Br\end{array}$

(*iv*) $CH_3-\overset{\overset{Cl}{|}}{\underset{\underset{Cl}{|}}{C}}-CH_3$ (*v*) $CH_3\underset{\underset{Cl}{|}}{C}H\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3$

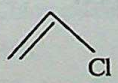
7.3. (*i*) neo-heptyl bromide (*ii*) tri-methylene dichloride (*iii*) propylene dichloride
(*iv*) Benzotrichloride (*v*) Benzyl iodide

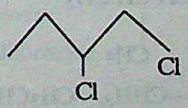
7.4. (*a*) These are (*i*) *n*-pentyl bromide (*ii*) iso-pentyl bromide (*iii*) sec-pentyl bromide
(*iv*) ter-pentyl bromide (*v*) neo-pentyl bromide

(*b*) (*i*) 

(*ii*) 

(*iii*)

(*iv*) 

(*v*) 

7.5. (*i*) Aryl halide (*ii*) Aralkyl halide (*iii*) Alkyl halide

7.6. $SOCl_2$ (Thionyl chloride)

7.7. ter-Butyl iodide ($(CH_3)_3CI$)

7.8. $CH_3CH_2CH(I)CH_3$ (sec-Butyl iodide)

7.9. CH_3CHCl_2 and CH_2ClCH_2Cl

7.10. Fluoboric acid

7.11. 1, 1, 1, 3, 3, 3-hexa iodo-2, 2-dimethyl propane

7.12. Silver acetate and Br_2/CCl_4

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7.13. (*i*) $CH_3\underset{\underset{OH}{|}}{C}HCH_2CH_3 + SOCl_2 \xrightarrow{\text{Pyridine}} CH_3\underset{\underset{Cl}{|}}{C}HCH_2CH_3$

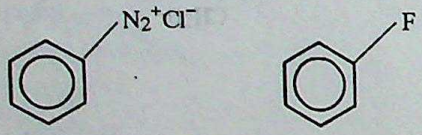
(*ii*) $2CH_3CH_2OH \xrightarrow{PCl_5} 2CH_3CH_2Cl \xrightarrow[\Delta]{Hg_2F_2} 2CH_3CH_2F + HgCl_2$

(*iii*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-OH \xrightarrow[160°]{H_2SO_4} CH_3-\overset{\overset{CH_3}{|}}{C}=CH_2 \xrightarrow[\text{M. Rule}]{HBr} CH_3-\underset{\underset{Br}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

7.14. (*i*) $CH_3\underset{\underset{Cl}{|}}{C}HCH_3$ (*ii*) $CH_3COOAg, CH_3Br + CO_2 + AgBr$

(*iii*) $CH_3\underset{\underset{Cl}{|}}{C}HCH_3$ (*iv*)

(*v*) (*vi*) $CH_3CH = CH_2, CH_2 = CH-\overset{\overset{Cl}{|}}{C}H_2$

(*vii*) 

$+ BF_3 + N_2$

7.15. $(CH_3)_3CCl$ **7.16.** (*iii*) < (*i*) < (*ii*)

7.17. $HC \equiv \overset{-}{C}\overset{+}{Na}$ (sod. acetylide) **7.18.** Iodomethane

7.19. 2-Butene **7.20.** Silver propionate (CH_3CH_2COOAg)

7.21. Magnesium (Mg) **7.22.** $CH_3CH_2CH_2CH_2Cl$

7.23. (*i*) N-Bromo succinamide (*ii*) Sodium ethoxide (*iii*) Br_2 in CCl_4

(*iv*) disodium acetylide ($Na\overset{+}{C}\equiv\overset{-}{C}Na$) (*v*) Na/dry ether

7.24. (*i*) Balz Schiemann reaction (*ii*) Hunsdiecker reaction (*iii*) Groove's process

(*iv*) Darzen's procedure (*v*) Corey-House Synthesis

7.25. (*i*) $(CH_3CH_2)_2N\underset{\cdot}{C}H_3 + HI$ (*ii*) $CH_3\overset{\overset{CH_3}{|}}{C}H\underset{\underset{CH_3}{|}}{C}HCH_3$ (*iii*) $CH_3CH_2C \equiv CH$

(*iv*) $CH_3\underset{\underset{OH}{|}}{C}HCH_3 + KCl$ (*v*) $CH_3-\underset{\underset{OH}{|}}{C}HH_3$, $CH_3\underset{\underset{Cl}{|}}{C}HCH_3$

7.26. CH_3Cl, Na, dry ether ; Wurtz Fittig reaction **7.27.** 2, 4, 6-trichlorobenzene

7.28. *o*-chlorobenzyl iodide **7.29.** Iodobenzene, Cu powder and dry ether.

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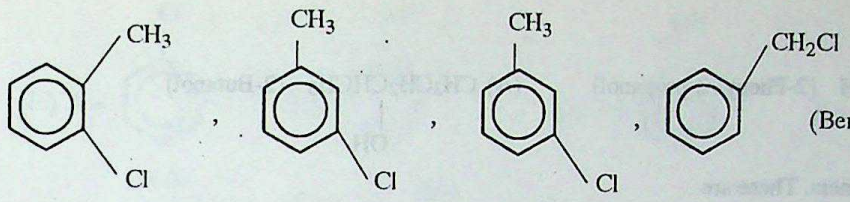
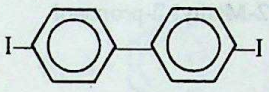
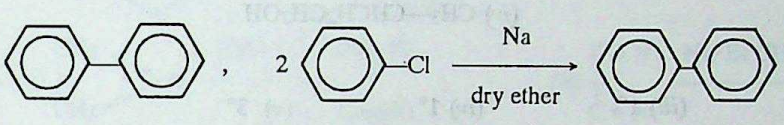
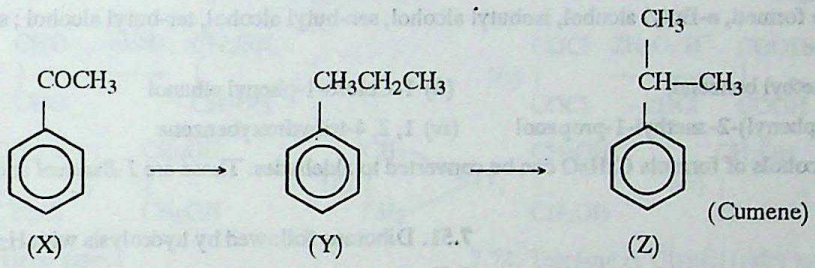
7.30. 

(Benzyl chloride is the weakest)

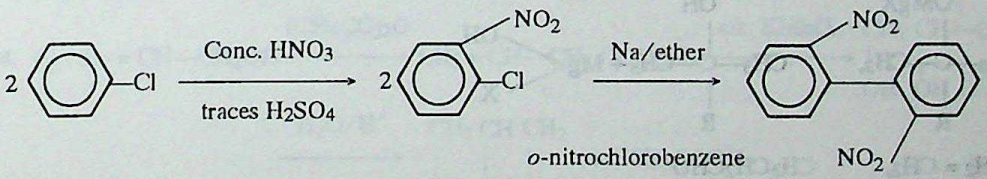
7.31. 

7.32. Benzyl chloride (or phenylchloromethane)

7.33. 

7.34. (*i*) 

(*ii*) $C_6H_5NH_2 \longrightarrow C_6H_5N_2^+Cl^- \longrightarrow C_6H_5I + N_2 + HCl$
(X) (Y) (Z)

7.35. 

7.36. (*i*) iso-propyl alcohol (*ii*) sec-Butyl alcohol (*iii*) sec-Butyl alcohol

7.37. (*i*) Hexachloro cyclohexane (*ii*) 1, 1, 2-trichloro ethene

7.38. (*i*) HC ≡ CH (acetylene) (*ii*) CCl_3NO_2 (Chloropicrin) (*iii*) Phenyl isocyanide

7.39. Carbon tetrachloride, *p, p'*-Dichlorodiphenyl trichloro ethane

7.40. Ethyl chloride reacts with alc. $AgNO_3$ to give white precipitate of AgCl whereas vinyl chloride does not

7.41. (*i*) $K_2CO_3 + 4KCl$ (*ii*) $CH_3N \rightleftharpoons C + 3KCl + 3H_2O$ (*ii*) $CH_2Cl_2 + HCl$

(*iv*) AgCl (*v*) $CH_2 = C\begin{matrix}Cl\\Cl\end{matrix}$

7.42. (*i*) Iodoform (*ii*) acetylene (*iii*) DDT
(*iv*) Chloropicrin (*v*) pyrene (*vi*) Westron
(*vii*) BHC (*viii*) chloretone (*ix*) phenyl isocyanide
(*x*) Ethylene dichloride

7.43. (*i*) $CH_3\underset{\underset{OH}{|}}{C}HCH_3$ (2-Propanol) (*ii*) $\begin{matrix}CH_2OH\\|\\CH_2OH\end{matrix}$ (1, 2-Ethanediol)

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(*iii*) $C_6H_5-C(CH_3)_2-OH$ (2-Phenyl-2-propanol) (*iv*) $CH_3CH_2CH(OH)CH_3$ (2-Butanol)

7.44. (*i*) 4 structural isomers. These are
(*i*) 1-Butanol (*ii*) 2-Butanol (*iii*) 2-Methyl-1-propanol and (*iv*) 2-Methyl-2-propanol

7.45. (*iii*) $CH_3-C(CH_3)_2-CH_2OH$ (*iv*) $CH_3-CH(CH_3)CH_2CH_2OH$

7.46. (*i*) 2° (*ii*) 1° (*iii*) 1° (*iv*) 1° (*v*) 3°

7.47. Four isomers are formed, *n*-Butyl alcohol, isobutyl alcohol, sec-butyl alcohol, ter-butyl alcohol ; sec-butyl alcohol is optically active

7.48. (*i*) 4-Hydroxy methyl benzenol (*ii*) 1-Chloro-1-phenyl ethanol
(*iii*) 1-(2′-chlorophenyl)-2-methyl-1-propanol (*iv*) 1, 2, 4-trihydroxybenzene

7.49. Only primary alcohols of formula C_4H_9O can be converted to aldehydes. These are *1-Butanol* and *2- Methyl-1-propanol*

7.50. $(CH_3)_3COH$ **7.51.** Diborane followed by hydrolysis with H_2O_2/OH^-

7.52. Cyclo pentanol **7.53.** Phenol is formed

7.54. *n*-propyl magnesium iodide

7.55. (*i*) $CH_3-C(OMgX)(R)-CH_3$, $CH_3-C(OH)(R)-CH_3 + Mg(OH)(X)$

(*ii*) $CH_2 = CH_2$, CH_3CH_2CHO

(*iii*) C_6H_5MgCl, C_6H_5OMgCl, $C_6H_5OH + Mg(OH)(Cl)$

7.56. *n*-pentyl alcohol, due to larger surface area **7.57.** O—H bond

7.58. isopropyl acetate ; $CH_3COOCH(CH_3)_2$ **7.59.** $(CH_3)_3C-OH$

7.60. No it forms H_2 and $C_2H_5\overset{-}{O}\overset{+}{Na}$ **7.61.** A = Cresol ; B = Benzyl alcohol

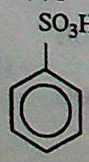
7.62. *p*-Cresol **7.63.** Salicylic acid

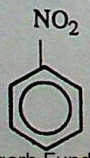
7.64. 2, 4, 6-trinitrophenol ; It is due to electron withdrawing effect of three nitro groups

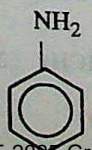
7.65. NaOH, it will dissolve phenol only

7.66. (*i*) H_2O, ethanol, phenol (*ii*) cresol, phenol, *p*-nitrophenol
(*iii*) Benzylalcohol, phenol, *o*-nitrophenol

7.67. (*i*) Phenol (*ii*) *p*-nitrophenol (*iii*) formic acid

7.68. (*i*) A = ; B = 

(*ii*) A = 

; B = 

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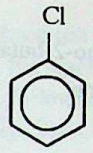
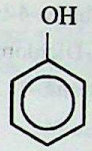
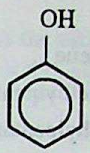
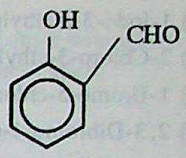
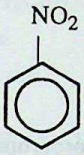
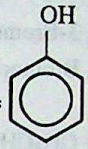
(*iii*) A = 

; B = 

(*iv*) A = 

; B = 

(*v*) A = 

; B = 

7.69. (*i*) $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>O \xrightarrow{H_2O/H^+} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$; (*ii*) $\begin{matrix} C\equiv N \\ | \\ C\equiv N \end{matrix} \xrightarrow{Na/Et\,OH} \begin{matrix} CH_2NH_2 \\ | \\ CH_2NH_2 \end{matrix} \xrightarrow{2HNO_2} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$

(*iii*) $\begin{matrix} CHO \\ | \\ CHO \end{matrix} \xrightarrow{NaBH_4} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$; (*iv*) $\begin{matrix} COCl \\ | \\ COCl \end{matrix} \xrightarrow[-2HCl]{2H_2O/H^+} \begin{matrix} COOH \\ | \\ COOH \end{matrix} \xrightarrow{LAH} \begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$

7.70. (*i*) $\begin{matrix} CH_2Cl \\ | \\ CH_2Cl \end{matrix}$; $\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$ (*ii*) $\begin{matrix} CH_2 \\ | \\ CH_2 \end{matrix}\!\!>O$; $\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$ (*iii*) $\begin{matrix} CH_2OH \\ | \\ CH_2OH \end{matrix}$; CH_3CHO

7.71. Ethylene glycol

7.72. Terelene or Glyptal (refer to chapter on polymers)

7.73. (*i*) Acrolein

(*ii*) HCHO + HCOOH

(*iii*) Glyceric acid

(*iv*) Trichloropropane

7.74. (*i*) $CH_2 = CH—CH_2OH \xrightarrow{(CH_3CO)_2O} CH_2 = CH—CH_2\,OOCCH_3 \xrightarrow{alk.\ KMnO_4} \begin{matrix} CH_2 & CH & —CH_2OOCCH_3 \\ | & | & \\ OH & OH & \end{matrix}$

$\xrightarrow{H_2O/H^+} \begin{matrix} CH_2 & CH & CH_2 \\ | & | & | \\ OH & OH & OH \end{matrix} + CH_3COOH$

(*ii*) $\begin{matrix} COOH \\ | \\ COOH \end{matrix}$ + glycerol $\xrightarrow{383\ K}$ HCOOH.

DESCRIPTIVE QUESTIONS

1. (*i*) $CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—Br$, 2-Bromo-2-methyl propane (*ii*) $CH_3—\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}—CH_2Cl$, 1-Chloro-2, 2-dimethyl propane

(*iii*) $CH_2 = CH—CH_2Br$, 3-Bromo-1-propene (*iv*) $CH_2 = CH—Cl$, Chloroethene

2. Three isomeric aromatic compounds are possible for $C_6H_4Cl_2$

(*i*) 1, 2-Dichlorobenzene (*ii*) 1, 3-Dichlorobenzene

(*iii*) 1, 4-Dichlorobenzene.

3. Eight isomers are possible, out of which three can exhibit enantiomerism.

4. (*i*) 1, 1-Dichloro-2-phenylethane (*ii*) 2-Chloro-2-phenyl butane

(*iii*) 3-Bromo-3-ethylpentane (*iv*) 1-Bromo-3-phenylpropane

(*v*) 1, 2-Dibromoethane (*vi*) 2-Chloro-3, 3-dimethylbutane

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(*vii*) 1-Iodo-3-methylpentane (*viii*) 1-Chloro-4-bromobutane

(*ix*) 2-Chloro-3-ethyl-1, 3-pentadiene (*x*) 1, 4-Dichloro-2, 3-dibromo-2-butane

(*xi*) 1-Bromo-5-chloro-3-chloromethylpentane (*xii*) 3-Bromo-1, 3, 5-hexatriene

(*xiii*) 2, 3-Dibromo-1-chloro-3-methylpentane.

5. Four isomers are possible

(*i*) 2-Bromotoluene (*ii*) 3-Bromotoluene

(*iii*) 4-Bromotoluene (*iv*) Bromophenylmethane

7. Four dichloro derivatives are possible for propane

(*i*) $CH_3CH_2CHCl_2$, 1, 1-Dichloropropane (*ii*) $CH_3CH(Cl)CH_2Cl$, 1, 2-Dichloropropane

(*iii*) $CH_2(Cl)CH_2CH_2(Cl)$, 1, 3-Dichloropropane (*iv*) $CH_3—C(Cl)_2—CH_3$, 2, 2-Dichloropropane.

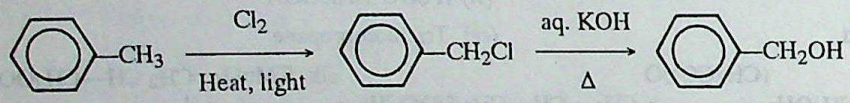
The isomer (*ii*) can exhibit enantiomerism.

13. Benzyl chloride is formed

18. (*i*) By addition of HBr

(*ii*) By addition of HBr in the presence of peroxides.

20. Follow the following steps :



27. Follow the following steps for different conversions :

(*i*) $NaOC_2H_5$ (*ii*) aq. KOH (*iii*) alc. KOH

(*iv*) H_2/Ni (*v*) NH_3(alc.) (*vi*) $AgNO_2$

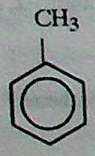
(*vii*) Na/ether.

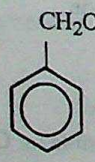
29. R—I > R—Br > R—Cl

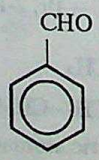
Explain in terms of strength of C—X bond.

31. (*i*) (A) $CH_3CH = CH_2$ (B) $CH_3CH(Br)CH_3$ (C) $CH_3CH(OH)CH_3$

(*ii*) (B) $CH_3CH(Cl)CH_3$ (A) $CH_3CH(OH)CH_3$ (C) $(CH_3)_2CH—CH(CH_3)_2$

(*iii*) (A) 

(B) 

(C) 

33. Follow the following steps :

(*i*) (*a*) alc. KCN (*b*) dil HCl (*ii*) (*a*) alc. KCN (*b*) H_2/Ni, Δ

(*iii*) (*a*) alc. KCN (*b*) conc. HCl (*iv*) (*a*) alc. NH_3 (in excess)

34. (*b*) $CH_3C \equiv CH \xrightarrow{NaNH_2} CH_3C \equiv CNa^+ \xrightarrow{C_2H_5Br} CH_3—C \equiv C—C_2H_5$

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35. *tert*-Butyl bromide would undergo elimination most readily as the alkene formed from it would be more stable. Moreover, the reaction in this case would take place *via* more stable intermediate carbocation.

37. Follow the following steps :

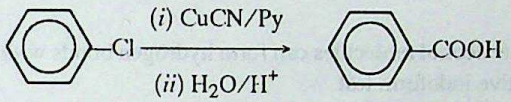
(*i*) (*a*) $CH_3Cl/AlCl_3$ (*b*) alk. $KMnO_4$ (*c*) $Cl_2/FeCl_3$

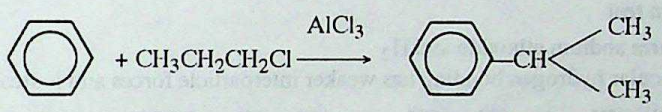
(*ii*) (*a*) $CH_3Cl/AlCl_3$ (*b*) $Cl_2/FeCl_3$ (*c*) alk. $KMnO_4$

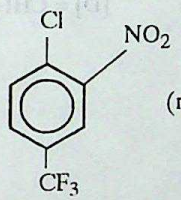
38. (*i*) Butane (*ii*) *n*-Butyl iodide (*iii*) *n*-Butylmagnesium chloride

(*iv*) *n*-Hexane

40. (*i*) $CH_3CH_2\underset{\underset{I}{|}}{C}HCH_3 \xrightarrow{KOH\ (alc.)} CH_3CH = CHCH_3$

(*ii*) 

(*iii*) 

41. 

(reactivity is more because of the presence of more electron withdrawing groups)

42. $CH_3—\underset{\underset{CH_3}{|}}{C}H—\underset{\underset{I}{|}}{C}H—CH_2—CH_3$

43. A is $CH_3CH_2CH_2Cl$; B is $CH_3CH_2CH_2CN$; C is $CH_2CH_2CH_2COOH$

44. (*i*) By $AgNO_3$ test, cyclohexylchloride will give positive test

(*ii*) By $AgNO_3$ test, benzylchloride will give positive $AgNO_3$ test

(*iii*) By $AgNO_3$ test, ethyl chloride will give positive test

(*iv*) By $AgNO_3$ test, allyl bromide will give positive test

(*v*) By Lassaigne's test

52. (*i*) Because it does not ionise to give chloride ions

58. (*i*) 2-Methyl-1-propanol (*ii*) 1, 2, 3-Propanetriol

(*iii*) Prop-2-yn-1-ol (*iv*) 2-Methyl-2-butanol

59. Five isomers are possible for C_7H_8O

60. (*i*) tertiary (*ii*) secondary

(*iii*) primary (*iv*) secondary

61. There are three such isomers

(*a*) 1-Propanol (*b*) 2-Propanol (*c*) Methoxyethane

62. (*i*) 4-Methylhex-2-en-3-ol (*ii*) 4-chloro-4-phenyl-1-butanol

64. There are four such alcohols. 2-Butanol can exhibit enantiomerism.

65. 2, 4-Dinitrophenol and 2, 4, 6-trinitrophenol are stronger acids than carbonic acid (H_2CO_3) due to the presence of electron withdrawing—NO_2 groups. Hence, they react with Na_2CO_3 to form their corresponding salts and dissolve in aq. Na_2CO_3 solution.

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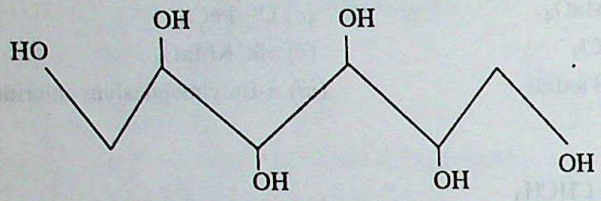
66. (*iv*) Due to electron withdrawing effect of phenyl group, the C—O bond in phenol is less polar, whereas in case of methanol the methyl group has electron releasing effect and hence C—O bond in it is more polar.

67. (*iii*) < (*ii*) < (*iv*) < (*i*)

69.



74. (*i*) Because of hydrogen bonding

(*ii*) With increase in molecular mass the non-polar alkyl group becomes more predominant

76. (*i*) $1^\circ > 2^\circ > 3^\circ$

(*ii*) Here —OH group is predominant and the alcohol molecules can form hydrogen bonds with water molecules

80. (*ii*) By iodoform test, ethanol will give positive iodoform test

(*iii*) By Lucas test or by iodoform test

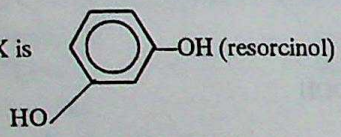
82. Ethanol reacts with sodium to form sodium ethoxide and H_2

83. (*ii*) *o*-Nitrophenol due intramolecular hydrogen bonding has weaker interparticle forces and is steam volatile

90. [A] = $CH_3CH(OH)CH_2CH_3$ [B] = $CH_3—C(=O)—CH_2—CH_3$ [C] = $CH_3—COOH$ [D] = CHI_3

91. (*i*) X is $CH_3—C(CH_3)=O$; Y is $CH_3—CH(CH_3)OH$; Z is $CH_3—CH(CH_2)Br$

(*ii*) X is C_6H_5Cl ; Y is C_6H_5OH

(*iii*) X is 

(resorcinol)

(*iv*) X is $(CH_3)_2C = CHCH_3$ (2-Methyl-2-butene).

92. (*i*) 1-Chloro-2-methylbutane (*ii*) 1, 3-Propanediol

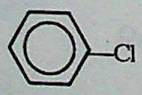
95. (*i*) 1, 2, 3-Propanetriol (*ii*) 2-Chloro-3-ethyl-1, 4-pentadiene

96. Follow the following steps :

(*i*) (*a*) Na (*b*) C_2H_5Br (*ii*) (*a*) CH_3MgI (*b*) H_2O/H^+

COMPLETING THE EQUATIONS

1. $CH_3CH_2CH_2Br$

2. 

3.

4. $C_6H_5—C(CH_3)_2—CH_3 + HCl$

5. $C_2H_5—O—C_2H_5 + NaBr$

6. $C_6H_5CH = CH—CH_3$, $C_6H_5CH(Br)—CH_2—CH_3$

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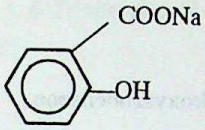
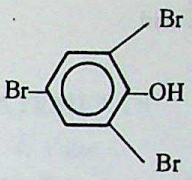
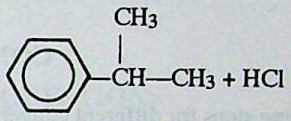
7. 

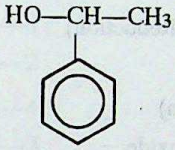
8. 

9. $CH_4 + Mg(OC_2H_5)I$

10. $C_6H_5Cl + POCl_3$

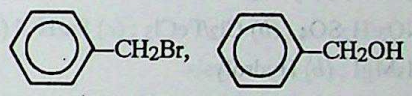
11. $(CH_3)_2C = CHCH_3$

12. 

13. 

14. $CH_3—\overset{CH_3}{\overset{|}{C}} = \overset{CH_3}{\overset{|}{C}}—CH_3$

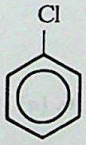
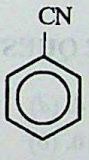
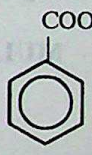
15. $CH_3—\overset{O}{\overset{\|}{C}}—CH_3$

16. 

17. $ClCH_2—CH_2OH$, $HOCH_2—CH_2OH$

19. $X = CH_3\underset{OH}{\underset{|}{C}}HCH_3$ $Y = CH_3CH = CH_2$ $Z = CH_3CH_2CH_2Br$

20. $X = CH_3CN$ $Y = CH_3CONH_2$

21. X =  Y =  Z = 

22. $X = CH_3CH_2Cl$ $Y = C_6H_5—CH_2CH_3$ $Z = C_6H_5—\underset{Cl}{\underset{|}{C}}H—CH_3$

23. $X = CH_3OH$ $Y = CH_3Br$ $Z = CH_3CH_2Cl$

24. $X = CH_3CH = CH_2$ $Y = CH_3COCH_3$ $Z = CH_3—\overset{OH}{\underset{C_2H_5}{C}}—CH_3$

WHAT HAPPENS WHEN

The important products formed are :

1. Ethyl isocyanide
2. 2-Methyl propene
3. Potassium formate
4. Phenolphthalein
5. Nitro glycerine
6. Sodium isopropoxide
7. Purple coloured complex
8. Ethyl iodide
9. Mixture of glyceryl aldehyde and dihydroxy acetone

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10. *p*-Hydroxybenzene sulphonic acid
11. 1, 3, 5-Trinitro benzene
12. Ethyl bromide
13. Iodobenzene
14. Coupling reaction, *p*-Hydroxyazobenzene
15. *p*-Bromophenol
16. diphenyl
17. propane is produced
18. 2-Methyl-2-butanol
19. Ethanal
20. Monosodium glycerolate and H_2

CONVERSIONS

Follow the following steps for different conversions :

1. (*a*) H_2SO_4/445 K ; (*b*) $KMnO_4$
2. (*a*) KCN (alc.) ; (*b*) H_2/Ni (Reduction)
3. (*a*) KCN (alc.) ; (*b*) dil. HCl (Complete hydrolysis)
4. (*a*) Cl_2/363 K
5. (*a*) $Cl_2/FeCl_3$; (*b*) HNO_3/H_2SO_4
6. (*a*) Na/ether (Wurtz reaction)
7. (*a*) alc. KOH (dehydrohalogenation) ; (*b*) HBr
8. (*a*) alc. KOH ; (*b*) HBr/peroxide
9. (*a*) $Cl_2/FeCl_3$; (*b*) Br_2/Fe
10. (*a*) HNO_3/H_2SO_4 ; (*b*) $Cl_2/FeCl_3$; (*c*) Sn/HCl (reduction of NO_2 group) (*d*) $NaNO_2$/HCl ; (*e*) CuBr/HBr
11. (*a*) CH_3MgI ; (*b*) Hydrolysis
14. (*a*) HBr ; (*b*) KCN (alc.) ; (*c*) H_2O/HCl ; (*d*) $LiAlH_4$
15. (*a*) B_2H_6 ; (*b*) Hydrolysis
16. (*a*) H_2SO_4 (dil.)/$HgSO_4$; (*b*) Br_2/NaOH(*aq*)
17. (*a*) HBr ; (*b*) Na/dry ether
18. Zn-Al/NaOH
19. $KHSO_4$
20. Conc. H_2SO_4 or Conc. H_3PO_4
21. (*a*) $K_2Cr_2O_7/H^+$ (*b*) NaOH (*c*) NaOH/CaO (*d*) Cl_2/heat (*e*) aq. KOH
24. (*a*) $C_2H_5Cl/AlCl_3$ (*b*) Cl_2/heat, light (*c*) aq. KOH.

MULTIPLE CHOICE QUESTIONS

1. (*b*) 2. (*c*) 3. (*b*) 4. (*d*) 5. (*c*) 6. (*a*)
7. (*b*) 8. (*a*) 9. (*b*) 10. (*b*) 11. (*d*)
12. (*d*) CH_3OH by reduction, C_2H_5OH by reaction into $CH_3MgI/H_2O/H^+$ and $CH_3CH_2CH_2OH$ by reaction with C_2H_5MgI followed by acidification.
13. (*b*) $CH_2 = CH—CH_2Cl$ after losing Cl gives a carbocation which is resonance stabilised.

$$CH_2 = CH—\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2—CH = CH_2$$

14. (*b*) 15. (*b*) 16. (*d*) 17. (*a*) 18. (*c*) 19. (*d*)
20. (*d*) 21. (*a*) 22. (*c*) 23. (*c*) 24. (*b*) 25. (*b*)
26. (*a*), (*c*) 27. (*b*), (*d*) 28. (*b*), (*d*) 29. (*a*), (*d*) 30. (*b*), (*c*) 31. (*a*), (*b*)
32. (*a*), (*d*) 33. (*a*), (*b*) 34. (*c*), (*d*) 35. (*b*), (*c*) 36. (*d*) 37. (*b*)
38. (*c*) 39. (*c*) 40. (*b*).

FILL IN THE BLANKS

1. $CH_3CH_2Cl + SO_2 + HCl$
2. HBr, KCN, dil. HCl
3. CO_2
4. CH_3CHO
5. 2, 4, 6-trinitrophenol
6. *n*-propylchloride
7. *o*-nitrophenol
8. Pyrogallol
9. 2-Phenylpropane
10. CCl_4
11. ethanol
12. hydrogen (or H_2)
13. Sabatier-Baumann
14. Fu-Butyl chloride
15. carbocations

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16. 2, 4, 6-Trinitrophenol **17.** more **18.** propanone
19. tertiary **20.** carbocations

TRUE/FALSE STATEMENTS

1. False	**2.** True	**3.** False	**4.** False	**5.** True	**6.** False
7. False	**8.** False	**9.** True	**10.** True	**11.** True	**12.** False
13. False	**14.** True	**15.** False	**16.** True	**17.** True	**18.** True
19. False	**20.** True				

MATCHING TYPE QUESTIONS

1. A—8 ;	B—5 ;	C—10 ;	D—9 ;	E—1 ;	F—3 ;
G—2 ;	H—4 ;	I—7 ;	J—6		
2. A—4 ;	B—5 ;	C—9 ;	D—1 ;	E—2 ;	F—10 ;
G—3 ;	H—6 ;	I—7 ;	J—8.		

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8

Organic Chemistry Based on Functional Groups—II

(Ethers, Aldehydes, Ketones, Carboxylic Acids and Derivatives of Carboxylic Acids)

LEARNING OBJECTIVES

In this Unit, we shall learn

— *to name ethers, aldehydes, ketones, carboxylic acids and their derivatives according to the IUPAC system ;*

— *the methods of preparation of the above classes of compounds ;*

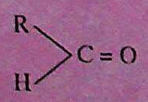
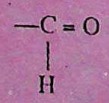
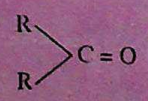
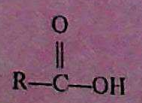
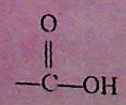
— *to correlate the variation in physical properties of the compounds with their structures ;*

— *the chemical properties of the above classes of compounds ;*

— *the correlation between the strength of carboxylic acids with their structures.*

In this unit, we shall study the chemistry of some families of organic compounds such as *ethers, aldehydes, ketones, carboxylic acids* and *the derivatives of carboxylic acids.* Our main attempt will be to be familiar with their general methods of preparation and their important general properties. The functional groups and names along with the general formulae of various families which will be discussed in this chapter are given in Table 8.1.

Table. 8.1. Names, Functional groups and General formulae of some families

Name of the family	*General structural formula*	*Functional group*
1. Ethers	R—O—R′	—O—
2. Aldehydes		
3. Ketones		> C = O
4. Carboxylic acids		

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Name of the family	*General structural formula*	*Functional group*
5. Derivatives of carboxylic acids		
(*i*) Acid halides or Acyl halides	$R-\overset{\overset{\displaystyle O}{\|}}{C}-X$ (X = F, Cl, Br, I)	$-\overset{\overset{\displaystyle O}{\|}}{C}-X$
(*ii*) Acid anhydrides	$R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R$	$-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-$
(*iii*) Esters	$R-\overset{\overset{\displaystyle O}{\|}}{C}-OR$	$-\overset{\overset{\displaystyle O}{\|}}{C}-O-$
(*iv*) Amides	$R-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$	$-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2$

R—refers to alkyl group.

ETHERS

Ethers are the compounds with general formula or $C_nH_{2n+2}O$ (same as monohydric alcohols). These are represented by general structure. **R—O—R′**. They may be regarded as *dialkyl derivatives* of water or *mono alkyl* derivatives of alcohols.

$$\underset{\text{Water}}{H-O-H} \xrightarrow[+\,2R]{-\,2H} \underset{\text{Ether}}{R-O-R} \xleftarrow[+\,R]{-\,H} \underset{\text{Alcohol}}{R-O-H}$$

They are also considered as *anhydrides of alcohols* because they can be obtained by the elimination of H_2O molecule from two alcohol molecules.

$$\underset{\text{Alcohols}}{R-OH + HO-R} \longrightarrow \underset{\text{Ether}}{ROR} + H_2O$$

The groups R and R′ in ether may either be same or different. In case these groups are same, the compounds are known as **simple ethers** or **symmetrical ethers.** On the other hand, if R and R′ groups are different, the compounds are called **mixed ether** or **unsymmetrical ethers.**

$C_2H_5-O-C_2H_5$ *Simple ether*

$C_2H_5-O-CH_3$ *Mixed ether*

Ethers may also be classified into two categories as *aliphatic ethers* and *aromatic ethers.* In **aliphatic ethers,** the groups R and R′ are both alkyl groups, whereas in **aromatic ethers,** one or both R and R′ groups are aryl groups. Ethers with one alkyl and one aryl group are also called *aryl alkyl ethers* or *phenolic ethers* whereas ethers with both aryl groups are called *diaryl ethers.* Some example are :

CH_3-O-CH_3 *Aliphatic ether*

Dimethyl ether

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$CH_3—O—C_6H_5$
Methyl phenyl ether

$C_6H_5—O—C_6H_5$
Diphenyl ether

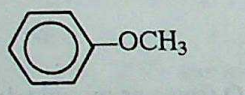
} *Aromatic ethers*

8.1. NOMENCLATURE OF ETHERS

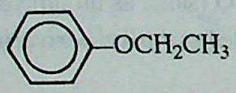
1. Common system. According to this system, the individual members are named according to alkyl groups attached to the oxygen atom. The two alkyl or aryl groups linked to oxygen atom are named in the alphabetic order followed by the word *ether*. In case of simple ethers, the prefix *di* is attached before the name of the alkyl group. Some examples are given below :

Simple ethers	**Mixed ethers**
$CH_3—O—CH_3$ *Dimethyl ether*	$CH_3—O—C_2H_5$ *Ethyl methyl ether*
$C_2H_5—O—C_2H_5$ *Diethyl ether*	$C_6H_5—O—C_2H_5$ *Ethyl phenyl ether*
$C_6H_5—O—C_6H_5$ *Diphenyl ether*	$CH_3—O—C(CH_3)_3$ *Tert-butyl methyl ether*

Some aromatic ethers have their special names. For example :



Anisole or (Methyl phenyl ether)



Phenetole or (Ethyl phenyl ether)

2. IUPAC System. According to IUPAC system, ethers are named as *alkoxyalkanes*. The larger alkyl group forms the part of parent chain while lower alkyl group constitutes *alkoxy* radical. Some examples are :

$CH_3—O—CH_3$ *Methoxymethane*

$CH_3—O—C_2H_5$ *Methoxyethane*

$CH_3—O—\overset{1}{C}H_2\overset{2}{C}H_2\overset{3}{C}H_3$ *1-Methoxypropane*

$C_2H_5—O—\overset{2}{C}H(\overset{1}{C}H)—\overset{3}{C}H_2—\overset{4}{C}H_3$ *2-Ethoxybutane*

The IUPAC names of some more ethers are being given as follows :

$C_2H_5—O—{}^2C(CH_3)_2$ (with $^1CH_3$ and $^3CH_3$)
2-Ethoxy-2-methylpropane

$CH_3\overset{3}{O}CH_2\overset{2}{C}H_2\overset{1}{C}H_2OCH_2CH_3$
1-Ethoxy-3-methoxypropane

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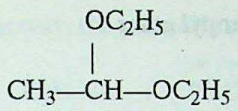
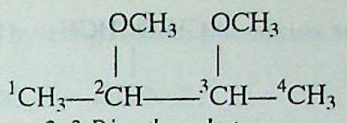
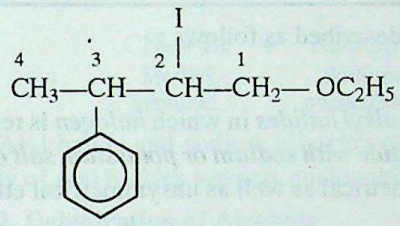


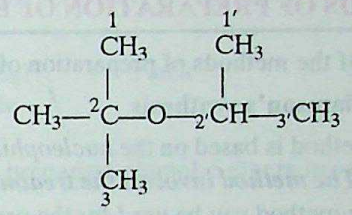
1, 1-Diethoxyethane



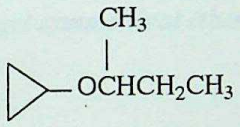
2, 3-Dimethoxy butane



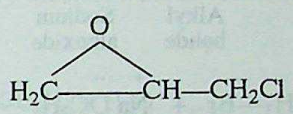
1-Ethoxy-2-iodo-3-phenylbutane



2-Methyl-2-(2′-propoxy) propane



2-Cyclo propoxybutane



1-chloro-2, 3-epoxypropane
(Epichlorohydrin)

REVIEW PROBLEMS

8.1. Give the structural formula of

(*i*) Chloromethyl methyl ether (*ii*) Diisopropyl ether
(*iii*) 1, 2-Dimethoxy ethane (*iv*) Bis (2-methoxyethyl) ether.

Ans. (*i*) $ClCH_2—O—CH_3$; (*ii*) $(CH_3)_2CHOCH(CH_3)_2$;
(*iii*) $CH_3OCH_2—CH_2OCH_3$; (*iv*) $(CH_3OCH_2CH_2)_2O$; *it is also called Diglyme*

8.2. Give structures of isomeric ethers with formula $C_4H_{10}O$. Also give their IUPAC names.

Ans. (*i*) $CH_3CH_2CH_2OCH_3$; *1-Methoxy propane*
(*ii*) $(CH_3)_2CHOCH_3$; *2-Methoxy propane*
(*iii*) $(CH_3CH_2)_2O$; *Ethoxyethane*

8.3. To which category of ethers do the following belong ?

(*i*) Phenetole (*ii*) 2-Methoxy-2-phenyl propane (*iii*) Di tertiary butyl ether.

Ans. (*i*) *phenolic ether* ; (*ii*) *unsymmetrical ether* ; (*iii*) *symmetrical ether*

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8.2. ISOMERISM IN ETHERS

Aliphatic ethers give two different type of isomers :

1. Functional isomers. Ethers are isomeric with alcohols.

For example, *dimethyl ether* (CH_3OCH_3) is isomeric with *ethyl alcohol* (C_2H_5OH).

2. Metamerism. Ethers with same molecular formula but different alkyl groups around oxygen are metamers. For example, an ether with formula $C_4H_{10}O$ give following metamers

$C_2H_5OC_2H_5$ Diethyl ether

$CH_3OCH_2CH_2CH_3$ Methyl propyl ether

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$$CH_3OCH(CH_3)_2 \quad \text{Methyl isopropyl ether}$$

8.3. METHODS OF PREPARATION OF ETHERS

Some of the methods of preparation of ethers are being described as follows :

1. Williamson's synthesis

This method is based on the *nucleophilic substitution of alkyl halides* in which *halogen* is replaced by *alkoxy group. The method involves the treatment of an alkyl halide with sodium or potassium salt of alcohol or phenol.* The method can be used for the preparation of symmetrical as well as unsymmetrical ethers.

$$\underset{\text{Alkyl halide}}{R{-}X} + \underset{\text{Sodium alkoxide}}{\overset{+}{Na}\,\overset{-}{O}R'} \longrightarrow \underset{\text{Ether}}{R{-}O{-}R'} + NaX$$

$$\underset{\text{Methyl bromide}}{CH_3{-}Br} + \underset{\text{Sodium ethoxide}}{\overset{+}{Na}\,\overset{-}{O}C_2H_5} \longrightarrow \underset{\text{Methoxy ethane}}{CH_3OC_2H_5} + NaBr$$

It may be noted that for preparing unsymmetrical ethers, a proper choice of the reactants is quite necessary. The halide used in this reactions should preferably be **primary** *because secondary and tertiary halides readily undergo elimination reaction in the presence of a strong base to form alkenes as the major product.* For example, if we have to prepare ethyl tertiary butyl ether, then we shall use *ethyl bromide* and *sodium tertiary butoxide.*

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{Sod. tert. butoxide}}{\overset{+}{Na}\overset{-}{O}{-}C(CH_3)_3} \longrightarrow \underset{\text{Ethy tert. butyl ether}}{C_2H_5{-}O{-}C(CH_3)_3} + NaBr$$

If we use tertiary butyl chloride and sodium ethoxide as reactants, the major products would be *isobutylene* and *ethanol*

$$\underset{\text{Tert. butyl chloride}}{CH_3{-}C(CH_3)_2{-}Cl} + \underset{\text{Sodium ethoxide}}{\overset{+}{Na}\overset{-}{O}C_2H_5} \longrightarrow \underset{\text{Isobutylene}}{CH_3{-}C{=}CH_2} + \underset{\text{Ethanol}}{C_2H_5OH} + NaCl$$

The preparation of methyl alkyl or ethyl alkyl ethers can also be done by using di-methyl sulphate or di-ethyl sulphate instead of alkyl halide.

For example,

$$\underset{\text{Sod. ethoxide}}{C_2H_5ONa} + \underset{\text{Dimethyl sulphate}}{(CH_3)_2SO_4} \longrightarrow \underset{\text{Ethyl methyl ether}}{C_2H_5OCH_3} + \underset{\text{Sod. methane sulphonate}}{CH_3SO_4^-Na^+}$$

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In the similar way, the **phenolic ethers** can be prepared by using **sodium phenoxide** and **alkyl halides.**

$$\underset{\text{Ethyl bromide}}{C_2H_5Br} + \underset{\text{Sodium phenoxide}}{\overset{+}{Na}\overset{-}{O}C_6H_5} \longrightarrow \underset{\text{Phenetole}}{C_2H_5OC_6H_5} + NaBr$$

$$\underset{\text{Methyl bromide}}{CH_3—Br} + \underset{\text{Sodium phenoxide}}{\overset{+}{Na}\overset{-}{O}C_6H_5} \longrightarrow \underset{\text{Anisole}}{CH_3OC_6H_5} + NaBr$$

Aryl halide and sodium alkoxide cannot be used for preparing phenolic ethers because of very less reactivity of aryl halides towards nucleophilic substitution.

2. Dehydration of Alcohols

This method involves heating of the excess of primary alcohol with concentrated sulphuric acid at 413 K to get symmetrical ether.

$$2C_2H_5OH \xrightarrow[413\ K]{Conc.\ H_2SO_4} \underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + H_2O$$

In this reaction alcohol has to be used in excess and the temperature has to be maintained around 413 K. If alcohol is not in excess or the temperature is higher, the alcohol will preferably undergo dehydration to yield alkene.

The use of secondary and tertiary alcohols in this reaction is avoided because they give alkenes as major products.

$$\underset{\text{Tert. butyl alcohol}}{CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}—OH} \xrightarrow{Conc.\ H_2SO_4} \underset{\text{Isobutylene}}{CH_3—\overset{\overset{CH_3}{|}}{C} = CH_2} + H_2O$$

This reaction cannot be employed to prepare unsymmetrical ethers.

In addition to the above method, the symmetrical ethers can also be obtained by passing vapours of alcohol under pressure over a heated catalyst like alumina, thoria, etc., at 520 K.

$$\underset{\text{Ethanol}}{2\ C_2H_5OH} \xrightarrow[520\ K]{Al_2O_3} \underset{\text{Ethoxyethane}}{C_2H_5OC_2H_5} + H_2O$$

3. By the action of diazomethane on alcohols or phenols

This method is used to prepare *methyl ethers* only. ***The process involves the treatment of alcohol or phenol with diazomethane (CH_2N_2) in the presence of fluoboric acid (HBF_4).***

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + \underset{\text{Diazo methane}}{CH_2N_2} \xrightarrow{HBF_4} \underset{\text{Methoxyethane}}{CH_3CH_2—OCH_3} + N_2$$

Similarly anisole can be prepared in excellent yield by this method

$$\underset{\text{Phenol}}{C_6H_5OH} + CH_2N_2 \xrightarrow{HBF_4} \underset{\text{Anisole}}{C_6H_5OCH_3} + N_2$$

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4. From alkenes. Ethers can also be prepared by ***addition of alcohols to alkenes in the presence of acids.*** For example, ethanol adds to isobutylene to give ter-butyl ethyl ether.

$$CH_3-\overset{CH_3}{\overset{|}{C}}=CH_2 + C_2H_5OH \xrightarrow{H_2SO_4} CH_3-\overset{CH_3}{\overset{|}{\underset{OC_2H_5}{\underset{|}{C}}}}-CH_3$$

Isobutylene Ethanol Ethyl tert-butyl ether

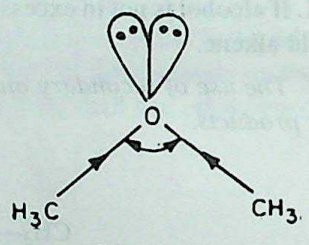
5. From Grignard reagent. By treating α-halo ethers with this reagent higher ethers can be obtained

$$CH_3OCH_2Cl + IMgCH_3 \longrightarrow CH_3OCH_2CH_3 + Mg\begin{matrix} I \\ Cl \end{matrix}$$

Monochloro-dimethyl ether Ethyl methyl ether Chloro magnesium iodide

8.4. STRUCTURE OF ETHERS

The central oxygen atom in ethers assumes sp^3 hybrid state. Two of the hybrid orbitals of oxygen are used in forming σ bonds with the surrounding alkyl groups. The other two sp^3 hybrid orbitals of oxygen contain lone pairs of electrons. The electron pairs (lone pairs as well as bond pairs) surrounding oxygen atom, assume tetrahedral arrangement. However, the bond angle around oxygen atom is not exactly equal to 109° 28′. The deviation in angle is caused by the repulsive interactions between the alkyl groups. Bulkier the alkyl groups, greater will be the repulsive interactions and consequently, larger will be deviation in angle. COC angle in dimethyl ether is 110°.



Dimethyl ether

Thus, ethers have ***bent structure*** and their dipole moment is greater than zero (μ > 0). Hence, their molecules are ***polar in nature***. For example, net dipole moment of diethyl ether is 1.18. D and that of dimethyl ether is 1.3 D.

8.5. PHYSICAL PROPERTIES OF ETHERS

1. Physical state. Dimethyl ether and ethyl methyl ether are gases at ordinary temperatures. The other lower homologues are colourless, pleasant smelling, volatile liquids with typical '*ether*' smell.

2. Boiling points. Ethers have much lower boiling points as compared to isomeric alcohols. Unlike alcohols, ether molecules are not associated by *hydrogen bonds*. The interparticle forces existing in their liquid states are weak *dipole-dipole* forces. However, the boiling points of ethers are close to corresponding alkanes with similar molecular masses as shown in Table 8.2.

Table 8.2. The Boiling Points of Ethers, Alkanes and Alcohols

Ether	*Mol. Mass*	*B.P. (K)*	*Alkane*	*Mol. Mass*	*B.P. (K)*	*Alcohol*	*Mol. Mass*	*B.P. (K)*
CH_3OCH_3	46	249	$CH_3CH_2CH_3$	43	231	C_2H_5OH	46	351
$C_2H_5OC_2H_5$	74	308	$CH_3(CH_2)_3CH_3$	72	309	n-C_4H_9OH	74	391
$C_6H_5OCH_3$	108	428	C_6H_5—C_2H_5	106	409	$C_6H_5CH_2OH$	108	478

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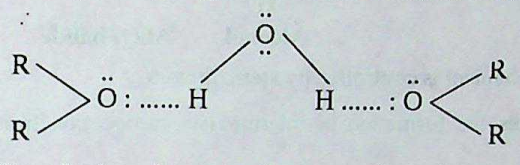
3. Solubility. The solubility of ethers is comparable to those of corresponding alcohols. For example, dimethyl ether and ethyl alcohol are both appreciably soluble in water. The *solubility of ethers is due to the capability of their molecules to form hydrogen bond with water molecules.*



However, solubility of ethers in water decreases from lower members to higher members. This is because of the relative increase in the hydrocarbon portion of the molecule which decreases the tendency of H-bond formation. Ethers are appreciably soluble in organic solvents like alcohol, benzene, acetone, etc.

8.6. CHEMICAL PROPERTIES OF ETHERS

Ethers are relatively inert compounds inspite of the presence of oxygen atom carrying two lone pairs of electrons in their molecules. These are not easily attacked by alkalies, dilute mineral acids, phosphorus pentachloride, metallic sodium, etc., under ordinary conditions. *It is because of this reason that these are used as solvents.* They undergo chemical reactions under specific conditions. Some of the reactions of ethers are being described as follows :

1. **Cleavage of C—O Bond**

Carbon oxygen bond in ethers can be cleaved by the use of reagents like *halogen acids, sulphuric acid* and *phosphorus pentachloride,* etc.

(*a*) **Cleavage with halogen acid.** Ethers can be cleaved by the use of hydroiodic acid or hydrobromic acid to give alkyl halide and alcohol.

$$\underset{\text{Ether}}{R—O—R} + \underset{\text{Halogen acid}}{HX} \xrightarrow{373\ K} \underset{\text{Alcohol}}{ROH} + \underset{\text{Alkyl halide}}{RX}$$

$$C_2H_5OC_2H_5 + HI \xrightarrow{373\ K} C_2H_5OH + C_2H_5I$$

In case *excess of HI* is used, the alcohol formed reacts further with halogen acid to form alkyl halide. The overall reaction can be written as

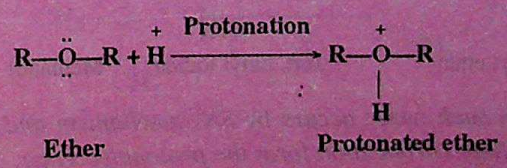
$$C_2H_5OC_2H_5 + \underset{\text{Excess}}{2HI} \xrightarrow{373\ K} 2C_2H_5I + H_2O$$

Mechanism of Cleavage by HX

(*a*) **SN^2 mechanism.** This involves protonation of ether by the acid followed by nucleophilic attack by *halide ion* on the protonated ether which results in formation of alcohol and alkyl halide. The various steps are

(*i*) $$HX \rightleftharpoons \overset{+}{H} + \overset{-}{X}:$$

(*ii*)



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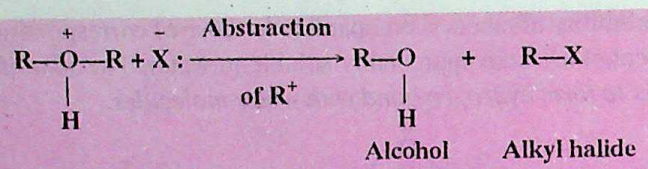

The reactivity through this mechanism is controlled by *steric factors.*

SN^1 Mechanism. This involves the formation of intermediate carbocation from the protonated ether as described below :

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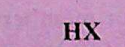

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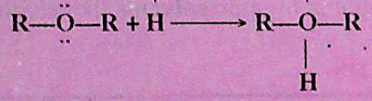

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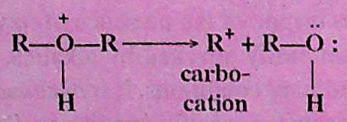

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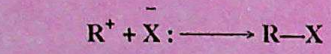
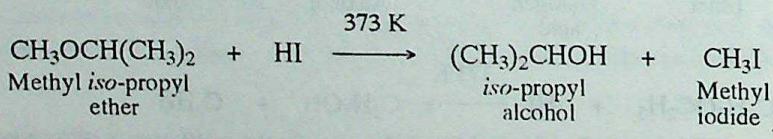


The reactivity through this mechanism is controlled by the *stability of intermediate carbocation.*

Site of Cleavage. *In case of unsymmetrical ethers, the site of cleavage depends on the nature of alkyl groups.*

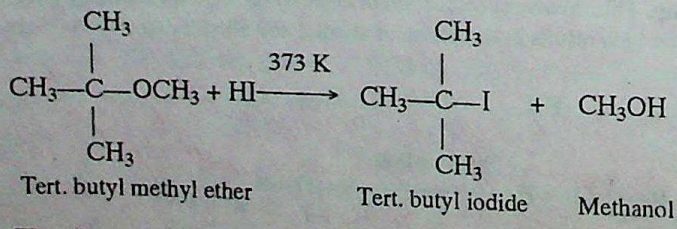
For example,

(i) If one group is methyl and other group is primary or secondary alkyl group. Then halide is formed from the *lower* alkyl group.



Explanation. *Cleavage of such ethers occurs by SN^2 mechanism and formation of product is controlled by steric factors. In this mechanism alkyl halide is formed by the attack of halide ion on the protonated ether. Now, bulkier the alkyl group, greater will be the steric hinderance for the approaching halide ion. Thus, halide ion preferably attacks the smaller alkyl group. Consequently, alkyl halide is formed from smaller alkyl group.*

(ii) If one group is methyl and other group is tertiary alkyl group, the main product is methyl alcohol and tertiary alkyl halide.



Explanation. *The cleavage in such cases occurs by SN^1 mechanism and formation of product is controlled by the stability of intermediate carbocation form the protonated ether. The tertiary carbocation being more stable forms more readily and subsequently produces tertiary halide.*

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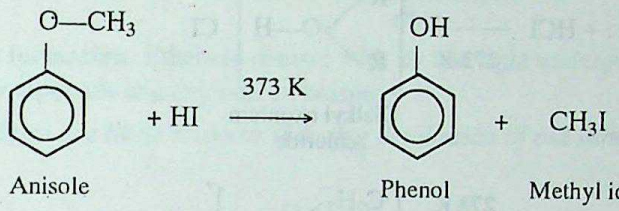
(*iii*) In case of ***phenolic ethers,*** the cleavage occurs with the formation of ***phenol*** and ***alkyl halide.*** *It is probably due to the fact that phenyl oxygen bond has a partial double bond character due to resonance. Therefore, its cleavage is relatively difficult as compared to alkyl oxygen bond.*



Diaryl ethers on the contrary are quite difficult to be cleaved even at high temperature.

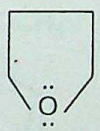
The **order of reactivity** of various halogen acids towards this reaction is :

HI > HBr > HCl *Order of reactivity*

If excess of HI is allowed to react with ethers under similar conditions, then both the alkyl groups form respective halides. It is due to the fact that alcohol formed during the reaction reacts further with HI to form alkyl halide.

$$\underset{\text{Diethyl ether}}{C_2H_5OC_2H_5} + \underset{\text{Excess}}{2HI} \xrightarrow{373\ K} \underset{\text{Ethyl iodide}}{2C_2H_5I} + H_2O$$

Cyclic ethers are readily cleaved by HBr or HI to form dihaloalkanes



$$+ \ 2HI \xrightarrow{373\ K} ICH_2CH_2CH_2CH_2I + H_2O$$

Tetrahydrofuran (THF) 1, 4-Diiodobutane

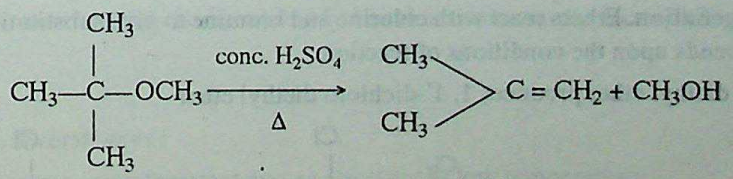
(*b*) **Cleavage with sulphuric acid.** On heating with *dilute sulphuric acid* under pressure, ethers are hydrolysed to alcohols

$$C_2H_5—O—C_2H_5 + H_2O \xrightarrow[\text{under pressure}]{\text{dil. } H_2SO_4} 2C_2H_5OH$$

If *concentrated sulphuric acid* is used, then the products are alcohol and ethyl hydrogen sulphate

$$C_2H_5—O—C_2H_5 + H_2SO_4 \xrightarrow{\text{Heat}} \underset{\text{Ethyl alcohol}}{C_2H_5OH} + \underset{\text{Ethyl hydrogen sulphate}}{C_2H_5OSO_2OH}$$

The secondary and tertiary ethers, however, form alkenes with conc. H_2SO_4.



Methyl-tert-butyl ether *Iso-Butylene*

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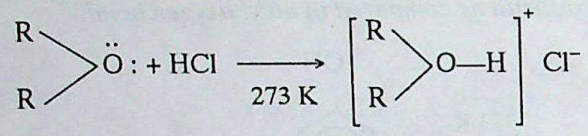
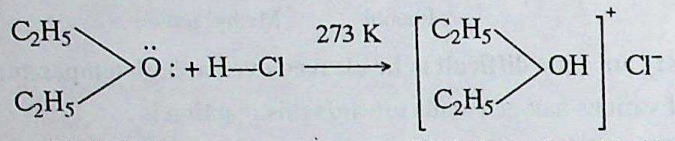
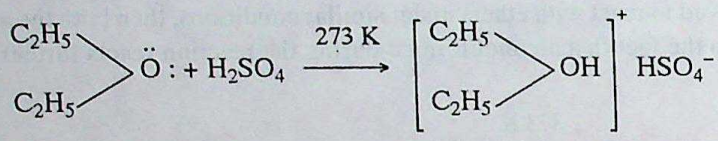
It may be noted that if ethers are treated with **cold conc. mineral acids,** they form respective **oxonium salts** instead of undergoing C—O cleavage.



Dialkyl oxonium chloride

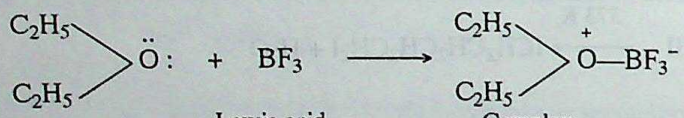


Diethyl ether — Diethyl oxonium chloride



Diethyl oxonium hydrogen sulphate

(*c*) **Reaction with Lewis acids.** Ethers are known to form complexes with Lewis acids. It is due to presence of unpaired electrons on O atom



Lewis acid — Complex

(*d*) **Cleavage with PCl_5.** In cold, PCl_5 has no action on ethers but on heating, phosphorus pentachloride also results in the cleavage of carbon-oxygen bond to form alkyl chlorides.

$$\underset{\text{Diethyl ether}}{C_2H_5—O—C_2H_5} + PCl_5 \xrightarrow{\text{Heat}} \underset{\text{Ethyl chloride}}{2C_2H_5Cl} + \underset{\text{Phosphoryl chloride}}{POCl_3}$$

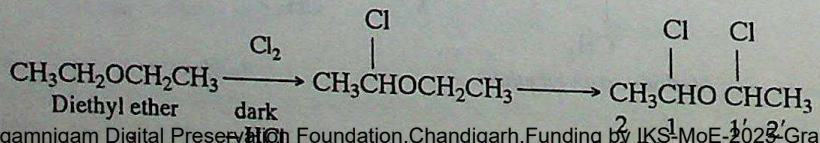
(*e*) **Reaction with acetyl chloride.** Ethers when heated with acetyl chloride in the presence of anhydrous zinc chloride, react to produce alkyl halide and ester.

$$\underset{\text{Ether}}{C_2H_5—O—C_2H_5} + \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow[\text{Heat}]{\text{Anhy. } ZnCl_2} \underset{\text{Ethyl chloride}}{C_2H_5Cl} + \underset{\text{Ethyl acetate}}{CH_3COOC_2H_5}$$

2. Reactions of the Alkyl Group

(*a*) **Halogenation.** Ethers react with chlorine and bromine to give substitution products. The extent of halogenation depends upon the conditions of reaction.

In dark, diethyl ether produces 1, 1′-dichloro diethyl ether



1, 1-Dichloro diethyl ether

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In the presence of **sunlight** all the hydrogens of ether are substituted by halogen atoms.

$$C_2H_5OC_2H_5 + 10Cl_2 \longrightarrow \underset{\text{Perchlorodiethyl ether}}{C_2Cl_5OC_2Cl_5} + 10HCl$$

(*b*) **Peroxide formation.** Ethers in contact with air and light undergo oxidation to produce peroxides which are unstable compounds and explode on heating.

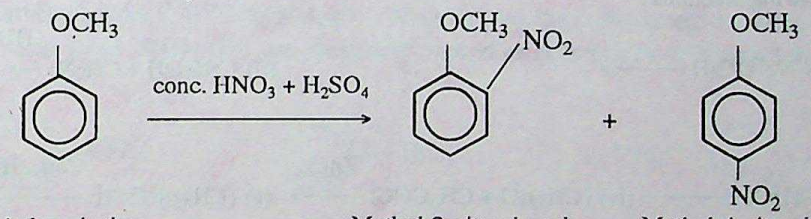
Serious accidents are likely to occur if during distillation of old samples of ethers, peroxides are not removed.

$$\underset{\text{Diethyl ether}}{CH_3CH_2OCH_2CH_3} \xrightarrow[\text{light}]{O_2} \underset{\text{1-Ethoxy ethylhydroperoxide}}{CH_3CH(OOH)—O—CH_2CH_3}$$

Presence of peroxides in ethers can be detected by the addition of freshly prepared $FeSO_4$ and KCNS. Appearance of red colour indicates peroxides. Ethers can be freed from peroxides by shaking with ferrous salt solution or distilling with concentrated H_2SO_4.

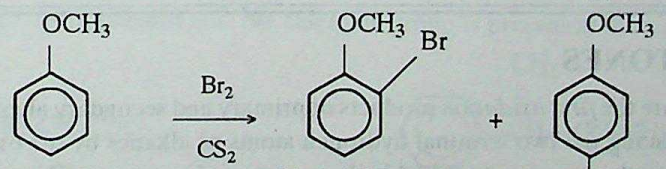
3. Ring Substitution in Aromatic Ethers

Aromatic ethers undergo electrophilic substitution in the ring at the *ortho*- and *para*-positions. For example, methyl phenyl ether gives a mixture of ortho and para nitro compounds when treated with a mixture of *concentrated nitric and sulphuric acids.*



Methyl phenyl ether or anisole — Methyl-2-nitrophenyl ether — Methyl-4-nitrophenyl ether

Similarly, *bromination* of anisole gives a mixture of *ortho* and *para* bromo derivatives.



Anisole — Methyl-2-bromo-phenyl ether — Methyl-4-bromo-phenyl ether

It may be *noted* that aromatic ethers are relatively *less reactive* towards electrophilic ring substitution than the phenols.

Uses of Ethers

Ethers find used in several ways :

(*i*) *Dimethyl ether* is used as refrigerant and as a solvent at low temperature.

(*ii*) *Diethyl ether* is used as solvent for organic reactions and also as an industrial solvent for oils, gums, resins, etc. It is also used as an extracting solvent.

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(*iii*) As anaesthetic in surgery.

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REVIEW PROBLEMS

8.4. How each of the following ethers can be prepared by Williamson's synthesis :

(*i*) $CH_3OCH_2CH_3$ (*ii*) $C_6H_5OCH_2CH_3$ (*iii*) $(CH_3)_3COCH_2C_6H_5$.

Hint. (*i*) *CH_3ONa and C_2H_5I or C_2H_5ONa and CH_3I.*

(*ii*) *Sodium phenoxide and ethyl iodide.* (*iii*) *Sodium tert. butoxide and benzyl chloride.*

8.5. How do the following react ?

(*i*) Benzyl phenyl ether and HI at 375 K (*ii*) Ethyl methyl ether and H_2SO_4 at 273 K

(*iii*) Isopropyl alcohol and CH_2N_2 in HBF_4 (*iv*) Di-isopropyl ether and excess of HI.

Hint. (*i*) *Phenol and benzyl iodide* (*ii*) *Oxonium hydrogen sulphate*

(*iii*) *2-Methoxy propane* (*iv*) *Isopropyl iodide.*

8.6. How do you account for the solubility of ethers in water and also in alcohols ?

Hint. *H-Bonding.*

8.7. An ether on treatment with excess of HBr give 1 mole of 1, 4-Dibromobutane per mole of ether. Identify the ether.

Ans. *Tetrahydrofuran.*

8.8. To prepare anisole, phenyl iodide cannot be taken as the starting material, why ?

Hint. *Due to resonance. The C—I bond acquires a double bond character.*

8.9. How will you prepare 2-Ethoxy propane by Williamson's method.

8.10. Complete the following reactions :

(*i*) $CH_3\underset{\underset{Cl}{|}}{C}HCH_3 + Na^+OC_2H_5 \longrightarrow$ (*ii*) $C_2H_5OH + CH_2N_2 \xrightarrow{HBF_4}$

(*iii*) $\overset{-}{C_6H_5O}\overset{+}{Na} + CH_3Cl \longrightarrow$ (*iv*) $(CH_3)_2O + CH_3COCl \xrightarrow{ZnCl_2}$ (*v*) $(CH_3)_3COCH_3 \xrightarrow[\Delta]{Conc.\ H_2SO_4}$

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ALDEHYDES AND KETONES

Aldehydes and ketones are the *first oxidation* products of primary and secondary alcohols respectively. Aldehydes are obtained by replacing the two terminal hydrogen atoms of alkanes by the oxygen atom while ketones are obtained by replacing the two non-terminal hydrogen atoms by oxygen. The common feature of both aldehydes and ketones is carbonyl group (> C = O) and, therefore, they are called **carbonyl compounds.**

8.7. NOMENCLATURE OF ALDEHYDES AND KETONES

(*a*) **Aldehydes. The trivial names** of aldehydes are derived from the names of the corresponding carboxylic acids (oxidation products of aldehydes) by replacing the suffix *ic acid* with *aldehyde*. Position of substituents in aldehyde chain, if any, is indicated by Greek letters α, β, γ, δ etc. The α-carbon is one which is directly attached to the *CHO* group.

$$\overset{\delta}{C}—\overset{\gamma}{C}—\overset{\beta}{C}—\overset{\alpha}{C}—CHO$$

In **IUPAC system**, aldehydes are named by replacing (*e*) from the corresponding name of alkane by suffix '*al*'. Therefore, aldehydes are called *alkanals.*

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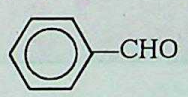
In case of higher aldehydes, the longest carbon chain is chosen and is numbered in such a way that the aldehyde group is given number one. The names of few aldehydes are given in Table 8.3.

Table 8.3. IUPAC and Trivial Names of Some Aldehydes

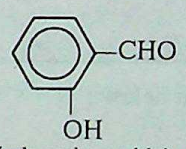
Formula	*Common Name*	*IUPAC Name*
$HCHO$	Formaldehyde	Methanal
CH_3CHO	Acetaldehyde	Ethanal
C_2H_5CHO	Propionaldehyde	Propanal
C_3H_7CHO	Butyraldehyde	Butanal
$CH_3CH(CH_3)CHO$	Isobutyraldehyde	2-Methylpropanal
$CH_3CH(Br)CH(CH_3)CHO$	β-Bromo-α-methyl butyraldehyde	3-Bromo-2-methylbutanal
$CH_3CH_2CH(Cl)CH(CH_2CH_3)CHO$	β-Chloro-α-ethyl-valeraldehyde	3-Chloro-2- ethylpentanal

Aromatic aldehydes are of two types :

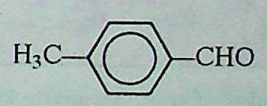
(*i*) Aldehydes in which aldehydic group (—CHO) is directly attached to benzene ring. The simplest member of the family is named as *benzaldehyde**. Now, in case the substituents are attached in *ortho, meta* or *para* positions then such aldehydes are generally named as derivatives of benzaldehyde. Some examples are :



Benzaldehyde

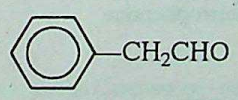


o-Hydroxybenzaldehyde or Salicylaldehyde

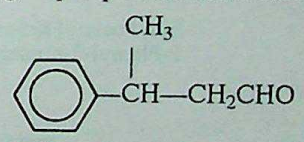


p-Methylbenzaldehyde or Tolualdehyde

(*ii*) In second type of compounds, the aldehyde group is present in the side chain. For example,



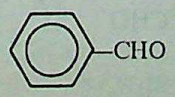
Phenylethanal



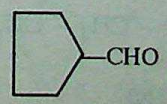
3-Phenylbutanal

(*b*) **Ketones.** Ketones are represented by the general formula RCOR′. They are termed as *simple ketones* if both R and R′ are same alkyl groups. On the other hand, they are termed as *mixed ketones* if R and R′ are different. In **common system, ketones** are named by using the names of alkyl groups attached to carbonyl group followed by the word '*ketone*'. For example, $CH_3COC_2H_5$ is *ethyl methyl ketone.*

*It may be noted that when formyl group (—CHO) is linked to the ring. The ring name is followed by ***cabaldehyde.*** Some examples are :



Benzene carbaldehyde



Cyclopentane carbaldehyde

However, the name benzaldehyde has been accepted as such by IUPAC.

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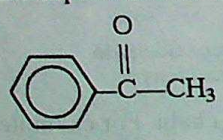
In the case of substituted ketones the positions of substituents are indicated by Greek letters, α, β, etc. (Trivial system) or numbers (IUPAC names). A few examples are given in Table 8.4.

According to the **IUPAC system**, the longest carbon chain carrying the carbonyl group is considered as the parent chain. This chain in numbered from one end such that the carbonyl carbon is given the lowest possible number. The name of the ketone is obtained by replacing '*e*' of the parent alkane by '*one*'. The positions of the carbonyl group and substituents are indicated by numbers. The names of some ketones are given in Table. 8.4.

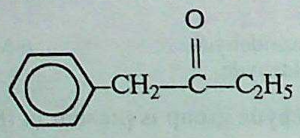
Table 8.4. Common and IUPAC Names of some Ketones

Molecular Formula	*Trivial Name*	*IUPAC Name*
$CH_3—CO—CH_3$	Acetone	Propanone
$CH_3—CH(CH_3)—CO—CH_3$	Methyl isopropyl ketone	3-Methyl-2-butanone
$CH_3—CH(CH_3)—CO—CH(CH_3)—CH_3$	Di-isopropyl ketone	2, 4-Dimethy-3-pentanone
$\beta\ \alpha\ \alpha'\ \beta'$ $CH_3CH(Cl)COCH_2CH_2(Cl)$	α, β′-Dichloro diethyl ketone	1, 4-Dichloro-3-pentanone
$CH_3CH(Cl)CO(Cl)(Cl)CH_3$	α, α′, α′-Trichlorodiethyl ketone	2, 2, 4-Trichloro-3-pentanone

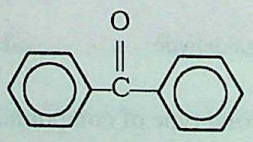
Examples of some aromatic ketones are given below :



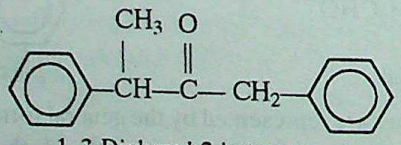
Methyl phenyl ketone or Acetophenone



Ethyl benzyl ketone or 1-Phenyl-2-butanone

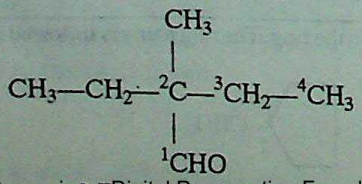


Diphenyl ketone or Benzophenone



1, 3-Diphenyl-2-butanone

The IPUAC names of some more aldehydes and ketones are given as follows :



2-Ethyl-2-methylbutanal

$^4CH_3{}^3CH = {}^2CH—{}^1CHO$

2-Butenal

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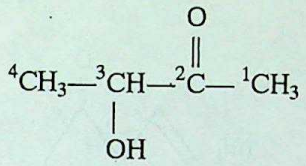
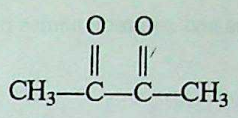
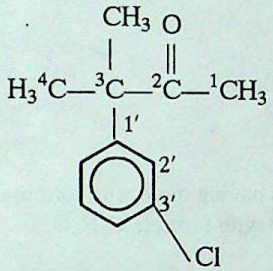


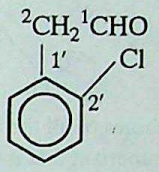
3-Hydroxy-2-butanone



2, 3-Butanedione



3-Methyl-3(3′-Chlorophenyl) -2-butanone



2- (2′-Chlorophenyl) ethanal

REVIEW PROBLEMS

8.11. Give the structures and IUPAC names of the following :

(*i*) Dibenzyl ketone (*ii*) Ethyl *neo*-pentyl ketone

(*iii*) Crotonaldehyde (*iv*) Phenyl acetaldehyde.

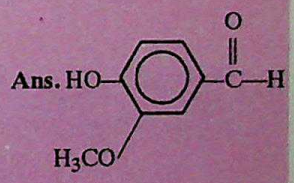
Ans. (*i*) $C_6H_5CH_2COCH_2C_6H_5$; *1, 3-Diphenyl-2- propanone*
(*ii*) $CH_3CH_2COCH_2C(CH_3)_3$; *5, 5-Dimethyl-2-hexanone*
(*iii*) $CH_3CH = CH—CHO$; *2-Butenal* (*iv*) $C_6H_5CH_2CHO$; *Phenyl ethanal.*

8.12. How many isomeric ketones are possible for 2, 2-Dimethyl propanal ?

Ans. *The molecular formula of 2, 2-Dimethyl propanal is $C_5H_{10}O$. The ketones possible are :*
(i) 2-Pentanone, (ii) 3- Pentanone, (iii) 3-Methyl-2-butanone

8.13. Vanillin is 4-hydroxy-3-methoxy benzaldehyde. Give its structure.

Ans.

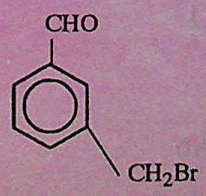


8.14. Write IUPAC names of the following :

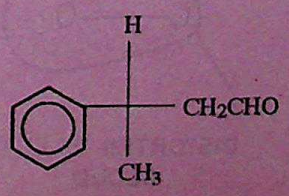
(*i*) $CH_3(CH_2)_2CH(CH_3)CH_2CHO$

(*ii*) $CH_3COCH(C_2H_5)CH_2CH_2Cl$

(*iii*)



(*iv*)



(*v*) $(CH_3)_2CHCOCH(CH_3)_2$.

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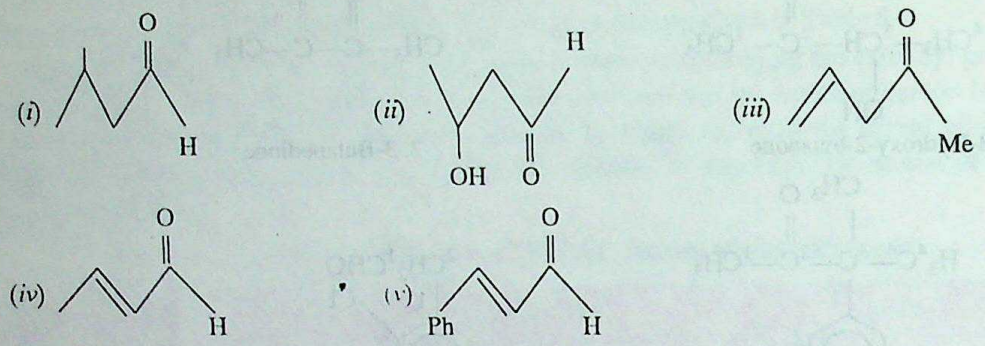
8.15. Write IUPAC names and common names of the following :



8.16. Give structures and IUPAC names of all the carbonyl compounds having molecular formula C_4H_8O.

8.17. Name the different kind of isomerism that is shown by compound with formula C_4H_8O.

8.18. Write correct IUPAC names of the following :

(*i*) Salicylaldehyde (*ii*) Acetylacetone (*iii*) Vinyl acetone

(*iv*) Benzyl phenyl ketone (*v*) Cinnamaldehyde.

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8.8. STRUCTURF OF CARBONYL GROUP

Both aldehydes and ketones have carbonyl group as the functional group. The carbonyl carbon is sp^2 hybridised and, thus, it has three sp^2 hybrid orbitals and one unhybridised *p*-orbital. It uses sp^2 hybrid orbitals to form three σ bonds, one with oxygen atom and remaining two with two other atoms or groups (**R** or **H**). All these three sigma bonds lie in same plane at the angle of 120°

The unhybridised *p*-orbital of carbonyl carbon forms π bond with oxygen atom by sidewise overlapping with half filled *p*-orbital of oxygen atom as shown in Fig. 8.1.

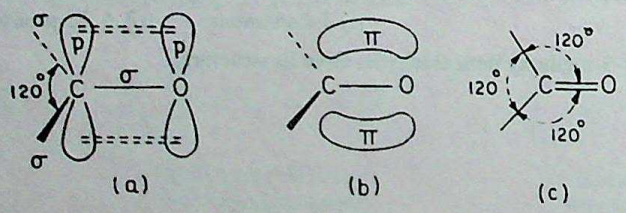

Fig. 8.1. Orbital picture of carbonyl group.

Since carbon and oxygen have different values of electronegativity, the bond between carbon and oxygen is polar. In fact, electron density around the oxygen atom is increased which causes the development of partial positive charge (δ+) on carbon and a partial negative charge (δ–) on oxygen atom. It has been shown in Fig. 8.2.

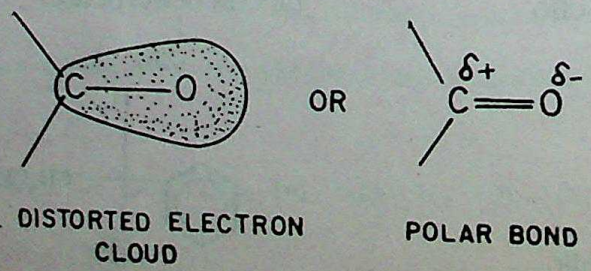

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Fig. 8.2. Polarised electron cloud in carbonyl group.

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The polar nature of carbonyl group is confirmed by the fact that dipole moments of aldehydes and ketones (2.3 to 3.02 D) are quite high.

Similarities and Differences between C = C and C = O bonds

The important similarities and difference between *carbonyl double bond (C = O) and ethylenic double bond (C = C)* have been discussed as follows :

Similarities. C = O and C = C are similar in following aspects :

(*i*) Both consist of a σ and a π bond.
(*ii*) In both, carbon atom assumes sp^2 hybrid state.
(*iii*) Both have planar structures.
(*iv*) Both undergo addition reactions.

Differences. C = O and C = C bonds are different in following aspects :

(*i*) C = O bond is polar while C = C bond is non-polar.
(*ii*) Their bond lengths and bond strengths are different.
(*iii*) C = O bond gives nucleophilic additions while C = C bond gives electrophilic additions generally.
(*iv*) Geometrical isomerism is possible in *C = C* bond but no such isomerism is possible in C = O bond.

8.9. GENERAL METHODS OF PREPARATION OF ALDEHYDES AND KETONES

Some of the general methods of preparation of aldehydes and ketones are as described below :

1. From Alcohols

Since aldehydes and ketones are first oxidation products of alcohols, hence, they can be prepared from alcohols by oxidation or dehydrogenation methods.

(*a*) **By direct oxidation.** *Aldehydes* are prepared by oxidation of *primary alcohols*. Acidified potassium permanganate or potassium dichromate is generally used as oxidising agents. Aldehydes are very susceptible to further oxidation to carboxylic acids. ***The reaction is controlled by distilling out aldehyde as soon as it is formed.***

$$\underset{\text{Primary alcohol}}{RCH_2OH} + [O] \longrightarrow \underset{\text{Aldehyde}}{RCHO} + H_2O$$

$$\underset{n\text{-Butyl alcohol}}{CH_3CH_2CH_2CH_2OH} + [O] \longrightarrow \underset{n\text{-Butyraldehyde}}{CH_3CH_2CH_2CHO} + H_2O$$

Collin's reagent *(chromium trioxide-pyridine complex) is a very good oxidising agent for converting 1° alcohols to aldehydes. This reagent checks the further oxidation of aldehydes to carboxylic acids. Collins reagent is used in non-aqueous medium like CH_2Cl_2.*

$$\underset{\text{Primary alcohol}}{RCH_2OH} \xrightarrow[CH_2Cl_2\text{ solvent}]{(C_5H_5N)_2CrO_3} \underset{\text{Aldehyde}}{RCHO} + H_2O$$

Ketones can be prepared by using similar oxidising agents from *secondary alcohols*.

$$\underset{\text{Sec. alcohol}}{\begin{matrix} R \\ R \end{matrix}\!\!>CHOH} + [O] \longrightarrow \underset{\text{Ketone}}{\begin{matrix} R \\ R \end{matrix}\!\!>C=O} + H_2O$$

$$\underset{sec\text{-Butyl alcohol}}{\begin{matrix} CH_3 \\ CH_3CH_2 \end{matrix}\!\!>CHOH} + [O] \longrightarrow \underset{\text{Ethyl methyl ketone}}{\begin{matrix} CH_3 \\ CH_3CH_2 \end{matrix}\!\!>C=O} + H_2O$$

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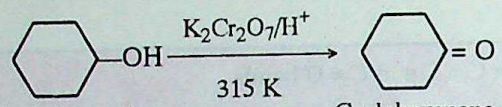
Similarly, cyclohexanol can be converted to cyclohexanone by an identical method



Cyclohexanol Cyclohexanone

(*b*) **By catalytic dehydrogenation.** When vapours of primary or secondary alcohols are passed over *copper* gauze at 573 K, they get dehydrogenated to form *aldehydes* or *ketones* respectively.

$$\underset{\textit{n}\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} \xrightarrow{Cu/573\ K} \underset{\text{Propionaldehyde}}{CH_3CH_2CHO} + H_2$$

$$\underset{\textit{iso}\text{-Propyl alcohol}}{(CH_3)_2CHOH} \xrightarrow{Cu/573\ K} \underset{\text{Acetone}}{(CH_3)_2C=O} + H_2$$

The dehydrogenation reaction is a better method of preparation because there is no risk of further oxidation of aldehyde.

2. From Acid Chlorides

Aldehydes are prepared from acid chlorides by reaction with H_2 in the presence of palladium catalyst supported on barium sulphate. The catalyst is partially deactivated (poisoned) by addition of sulphur or quinoline. This partial poisoning is done in order to avoid the *further reduction of aldehydes to alcohols*. This reaction is called **Rosenmund's reaction.**

$$\underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} + H_2 \xrightarrow[\text{(Boiling xylene)}]{Pd,\ BaSO_4,\ S} \underset{\text{Aldehyde}}{R-\overset{O}{\overset{\|}{C}}-H} + HCl$$

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \xrightarrow{Pd,\ BaSO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + HCl$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + H_2 \xrightarrow{Pd,\ BaSO_4} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

Ketones are obtained by reacting *acid chlorides* with *dialkyl cadmium.*

$$2RCOCl + CdR_2' \longrightarrow \underset{\text{Ketone}}{2RCOR'} + CdCl_2$$

$$\underset{\text{Ethanoyl chloride}}{2CH_3COCl} + \underset{\text{Dimethyl cadmium}}{(CH_3)_2Cd} \longrightarrow \underset{\text{Propanone (Acetone)}}{2CH_3COCH_3} + CdCl_2$$

Ketones *cannot be obtained by Rosenmund's reaction. Another point that must be kept in mind is that ketones cannot be obtained by the reaction of acid chlorides with Grignard's reagent. It is because the ketone obtained would further react with Grignard's reagent to form tertiary alcohol.*

$$\underset{\text{Acid chloride}}{CH_3-\overset{O}{\overset{\|}{C}}-Cl} + \underset{\text{Methyl mag. chloride}}{ClMgCH_3} \longrightarrow CH_3-\overset{O}{\overset{\|}{C}}-CH_3 + MgCl_2$$

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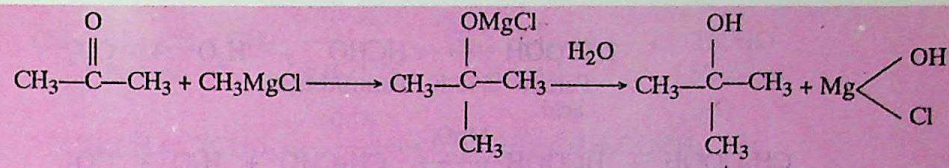
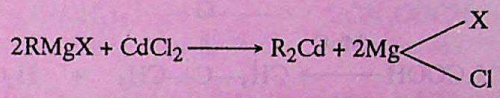
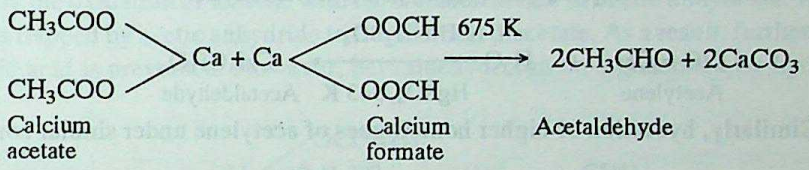


To avoid this, **dialkyl cadmium** is used. *Dialkyl cadmium is prepared by the reaction between Grignard's reagent and cadmium chloride.*

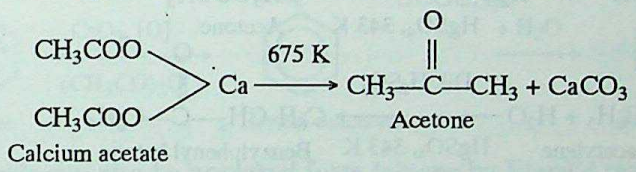


3. From Fatty Acids

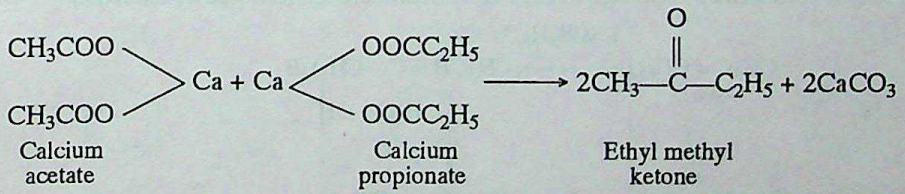
(*a*) **By heating calcium salt of fatty acids.** *Aldehydes* are obtained by heating calcium salts of fatty acids with calcium formate to about 675 K.



Ketones are formed by distilling calcium salt of the fatty acid alone.

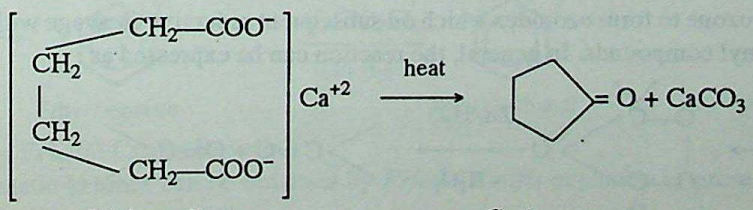


Similarly, *mixed ketones* can also be obtained by similar reactions.



It must be noted here that the yield of aldehydes and ketones is poor for this reaction because a number of other products may also be obtained. For example, the reaction of calcium acetate and calcium formate also gives acetone and formaldehyde along with acetaldehyde.

This method can also be employed for the preparation cyclic ketones. For example,



(*b*) **By passing vapours of fatty acids over manganous oxide.** In this method, formic acid alone gives formaldehyde. Acetic acid gives acetone and the mixture of two acids *i.e.*, formic and acetic acids produce acetaldehyde.

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$$\underset{\text{Formic acid}}{2HCOOH} \xrightarrow[575\ K]{MnO} \underset{\text{Formaldehyde}}{HCHO} + H_2O + CO_2$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Formic acid}}{HCOOH} \xrightarrow[575\ K]{MnO} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2O + CO_2$$

$$\underset{\text{Acetic acid}}{2CH_3COOH} \xrightarrow[575\ K]{MnO} \underset{\text{Acetone}}{CH_3-\overset{\overset{O}{\|}}{C}-CH_3} + H_2O + CO_2$$

4. From Alkynes

Aldehydes and ketones can be prepared by *hydration of alkynes*. For example, hydration of acetylene in the presence of dilute H_2SO_4 and $HgSO_4$ gives acetaldehyde.

$$\underset{\text{Acetylene}}{HC \equiv CH} + H_2O \xrightarrow[HgSO_4,\ 343\ K]{\text{Dil. } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

Similarly, hydration of higher homologues of acetylene under similar conditions give ketones

$$\underset{\text{Allylene}}{CH_3-C \equiv CH} + H_2O \xrightarrow[HgSO_4,\ 343\ K]{\text{Dil. } H_2SO_4} \underset{\text{Acetone}}{CH_3COCH_3}$$

$$\underset{\text{Diphenyl acetylene}}{C_6H_5C \equiv CC_6H_5} + H_2O \xrightarrow[HgSO_4,\ 343\ K]{\text{Dil. } H_2SO_4} \underset{\text{Benzylphenyl ketone}}{C_6H_5CH_2-\overset{\overset{O}{\|}}{C}-C_6H_5}$$

Non terminal alkynes can also be converted to ketones by hydroboration followed by oxidation

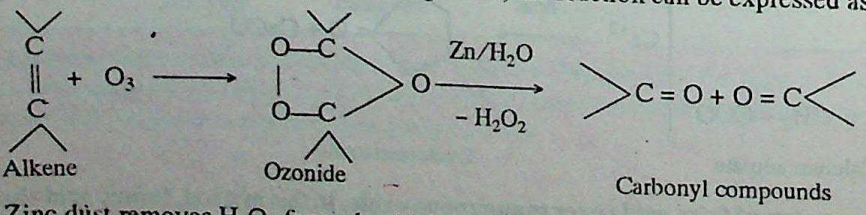
$$CH_3C \equiv CCH_3 \xrightarrow{1/2\ B_2H_6} (CH_3CH = C-CH_3)_3B$$

$$\downarrow H_2O_2,\ OH^-$$

$$\left[CH_3CH = \underset{\underset{OH}{|}}{C}CH_3\right] \longrightarrow CH_3CH_2\overset{\overset{O}{\|}}{C}CH_3$$

5. By Reductive Ozonolysis of Alkenes

Alkenes react with ozone to form ozonides which on subsequent reductive cleavage with *zinc dust* and *water* or H_2/Pd give carbonyl compounds. In general, the reaction can be expressed as :



Zinc dust removes H_2O_2 formed, which otherwise can further oxidise the aldehydes formed to acids. Thus, by starting with suitable alkene, the desired aldehyde or ketone can be formed. Some examples are being given below :

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(*a*) $CH_3(CH_2)_2CH = CH_2 \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} CH_3(CH_2)_2CHO + HCHO$

1-Pentene → Butanal + Methanal

(*b*) $CH_3CH = C(CH_3)_2 \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} CH_3CHO + CH_3COCH_3$

2-Methyl-2-butene → Ethanal + Propanone

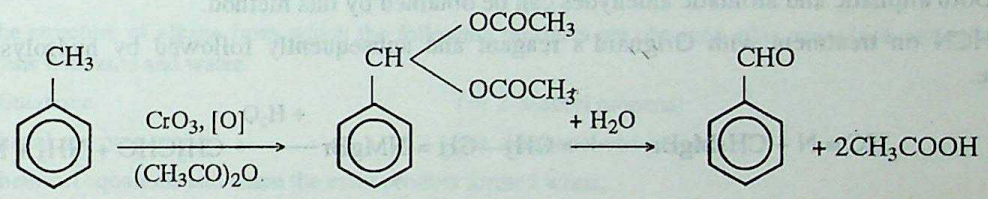
(*c*) $(CH_3)_2C = C(CH_3)_2 \xrightarrow[(ii)\ H_2O/Zn]{(i)\ O_3} 2CH_3COCH_3$

2, 3-Dimethyl-2-butene → Propanone

8.10. PREPARATION OF AROMATIC ALDEHYDES AND KETONES

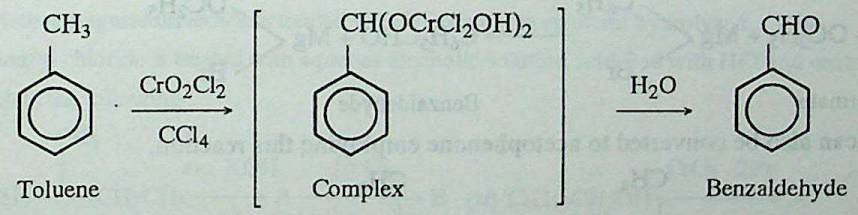
1. By Oxidation of Alkyl Benzenes

Aromatic aldehydes are obtained by the oxidation of side chain in the aromatic ring. For example, benzaldehyde is obtained by the oxidation of toluene with *chromium trioxide* in *acetic anhydride*. In this case the benzaldehyde formed is trapped by acetic anhydride to form benzal diacetate. As a result, further oxidation of benzaldehyde to benzoic acid is prevented. However, benzaldehyde can be regenerated by hydrolysis of benzal diacetate.



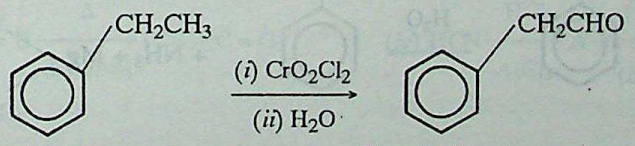
Toluene → Benzal diacetate → Benzaldehyde

Benzaldehyde can also be prepared form toluene by Etard's reaction. The reaction involves the oxidation of toluene with *chromyl chloride* (CrO_2Cl_2) in CCl_4.



Toluene → Complex → Benzaldehyde

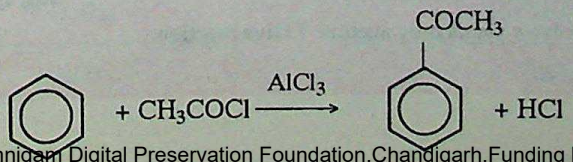
In the case of side chains bigger than CH_3 group the end carbon atom of the chain is oxidised by CrO_2Cl_2 to —CHO group.



Ethyl benzene → Phenyl ethanal

2. By Friedel Crafts Reaction

Aromatic ketones can be obtained by *Friedel Crafts acylation* in presence of anhydrous aluminium chloride.



Benzene + Acetyl chloride → Acetophenone

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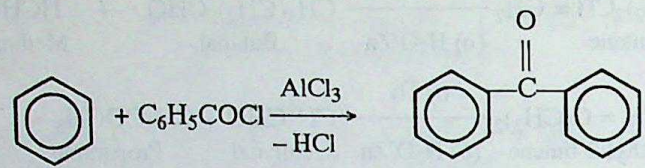
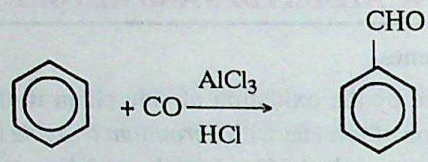
Similarly, treatment of benzene with benzoyl chloride in the presence of $AlCl_3$ gives benzophenone



Benzene Benzoyl chloride Benzophenone

3. By Gattermann Koch Reaction

In this method aromatic aldehydes are prepared by formylation of aromatic ring with carbon monoxide



Benzaldehyde

4. From Grignard's Reaction

Both aliphatic and aromatic aldehydes can be obtained by this method.

HCN on treatment with Grignard's reagent and subsequently followed by hydrolysis yields an aldehyde.

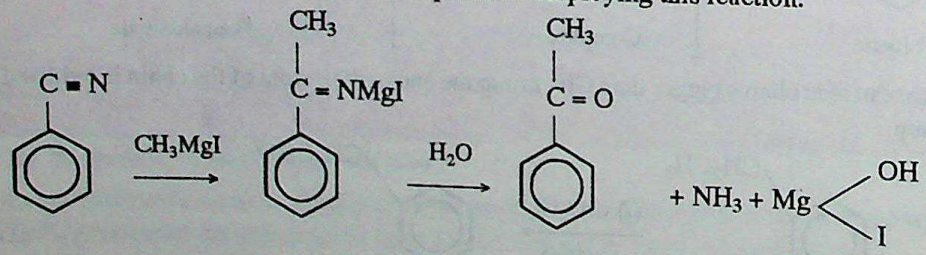
$$HC \equiv N + CH_3MgBr \longrightarrow CH_3{-}CH = NMgBr \xrightarrow{+H_2O} CH_3CHO + NH_3 + Mg\begin{matrix} OH \\ Br \end{matrix}$$

Similarly benzaldehyde can be obtained in a good yield by treating ethyl formate with phenyl magnesium bromide.

$$H{-}\overset{\overset{O}{\|}}{C}{-}OC_2H_5 + Mg\begin{matrix} C_6H_5 \\ Br \end{matrix} \longrightarrow C_6H_5CHO + Mg\begin{matrix} OC_2H_5 \\ Br \end{matrix}$$

Ethyl formate Benzaldehyde

Benzonitrile can also be converted to acetophenone employing this reaction.



REVIEW PROBLEMS

8.19. What is the hybrid state of carbon 1 and 2 in ethanal ? **Ans.** *sp^2 and sp^3 respectively*

8.20. Which alkene on reductive ozonolysis yields only acetone ? Give reaction.

Hint. *2, 3 Dimethyl-2-butene*

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8.21. Which aldehydes are formed by reductive ozonolysis of 1, 3-pentadiene ?

Hint. *HCHO,* $\begin{array}{c} CHO \\ | \\ CHO \end{array}$ *(glyoxal) and* CH_3CHO

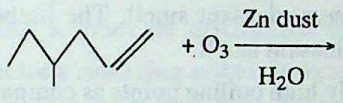
8.22. Giving chemical reaction, name the product when the following reagents are allowed to react :

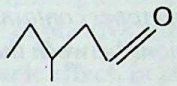
(*i*) 2-Butanol with Copper at 575 K (*ii*) Benzoyl chloride and diethyl cadmium

(*iii*) Ethyl benzene and chromyl chloride.

Hint. (*i*) *2-Butanone ;* (*ii*) *Ethyl phenyl ketone ;* (*iii*) *Phenyl ethanal*

8.23. What product is obtained in the following reaction.



Hint. 

+ HCHO

8.24. Calcium salt of an acid X on dry distillation with calcium formate produces isobutyraldehyde as the product. What is X ?

8.25. Give the structure of alkene from which the following products are obtained after ozonolysis and subsequent hydrolysis with zinc and water.

(*i*) 2-Butanone (*ii*) 2-Methyl propanal

(*iii*) Ethanal and propanone (*iv*) Methanal and propanal.

8.26. Give chemical equations and name the main product formed when,

(*i*) Ethylalcohol is mixed with air and passed over Ag catalyst at 520 K.

(*ii*) Benzoyl chloride is treated with Lithium tri ter-butoxy aluminium hydride.

(*iii*) Isopropylidene chloride is treated with caustic potash.

(*iv*) Methyl magnesium iodide is treated with HCN and the resultant hydrolysed.

(*v*) Benzyl chloride is treated with aqueous alcoholic solution acidified with HCl and urotropine

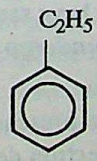
8.27. Complete the following :

(*i*) $CH_3-\underset{Cl}{\overset{CH_3}{C}}-CH_2CH_3 \xrightarrow{\text{alc. KOH}} A \xrightarrow[(ii)\ Zn/H_2O]{(i)\ O_3} B$

(*ii*) $C_6H_{13}CH_2OH \xrightarrow[CH_2Cl_2]{CrO_3 \cdot 2Py} A$

(*iii*) $A \xrightarrow{CaCO_3} B \xrightarrow[\text{dry distil}]{\Delta} (CH_3)_2C=O$

(*iv*) $HCN \xrightarrow[AlCl_3]{HCl} A \xrightarrow[(ii)\ H_2O/H^+]{(i)\ C_6H_6,\ \Delta} B$

(*v*) 

$\xrightarrow{CrO_2Cl_2} A$

(*vi*) $CH_3C \equiv CH \xrightarrow{B_2H_6} A \xrightarrow[H_2O_2]{H_2O,\ OH^-} B$

(*vii*) $A \xrightarrow[HCl]{SnCl_2} B \xrightarrow[H_2O_2]{H_2O,\ OH^-} CH_3CHO$

(*viii*) $C_6H_6 \xrightarrow[AlCl_3]{CH_3CH_2CH_2Cl} A \xrightarrow[H_2SO_4]{K_2Cr_2O_7} B$

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(ix) $A \xrightarrow[H_2SO_4]{HgSO_4} B \xrightarrow{[O]} CH_3CO_2H$

(x) $CH_3\underset{\underset{I}{|}}{CH}CH_3 \xrightarrow{\text{alc. KCN}} A \xrightarrow[(ii)\ H_2O,\ OH,\ H_2O_2]{(i)\ SnCl_2/HCl} B$

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8.11. PHYSICAL PROPERTIES OF ALDEHYDES AND KETONES

1. Physical state. Most of the aldehydes (except formaldehyde which is a gas) are liquids at room temperature. The lower ketones are colourless liquids and have pleasant smell. The higher members are colourless solids. Aromatic ketones are usually solids with a pleasant smell.

2. Boiling points. Aldehydes and ketones have relatively high boiling points as compared to hydrocarbons of comparable molecular masses. *It is due to the reason that aldehydes and ketones contain polar carbonyl group and, therefore, they have stronger intermolecular dipole dipole interactions between the opposite ends of C = O dipoles.*

These *dipole-dipole* interactions are however, weaker than intermolecular H-bonding in alcohols. Consequently, boiling points of aldehydes and ketones are relatively lower than the alcohols of comparable molecular masses.

Compound	CH_3CH_2CHO	$CH_3CH_2CH_2OH$	$CH_3CH_2CH_2CH_3$
	Propanal	*1-Propanol*	*Butane*
Molecular mass	*58*	*60*	*58*
b.p. (K)	*322*	*371*	*309*

Ketones are relatively more polar than their corresponding isomeric aldehydes due to the presence of two electron repelling alkyl groups around the carbonyl carbon. Thus, boiling points of ketones are slightly higher than those of isomeric aldehydes.

Compound	CH_3COCH_3	CH_3CH_2CHO
	Propanone	*Propanal*
Molecular mass	*58*	*58*
Dipole moment (μ)	*2.88 D*	*2.80 D*
b.p. (K)	*329*	*322*

3. Solubility. The lower members of aldehydes and ketones (up to four carbon atoms) are soluble in water. *It is due to their capability of forming hydrogen bonds with water molecules.* The solubility of these compounds in water decreases with the increase in the size of alkyl group. *It is because of the increase in the magnitude of non-polar part in the molecule.* However, higher homologues are soluble in organic solvents.

8.12. CHEMICAL PROPERTIES

Aldehydes and ketones are highly reactive compounds. Since both these classes have same functional group, they show a large number of common reactions. ***Both aldehydes and ketones undergo nucleophilic addition reactions.***

Explanation. The reactive nature of aldehydes and ketones is because of the presence of a polar carbonyl group. As the oxygen atom is more electronegative, therefore, it pulls the electron density around itself acquiring a partial negative charge (δ–) whereas a partial positive charge (δ+) is developed on the carbon atom.

The positively charged carbon atom of carbonyl group is then readily attacked by the nucleophilic species for initiation of the reaction. This leads to the formation of an intermediate cation which further

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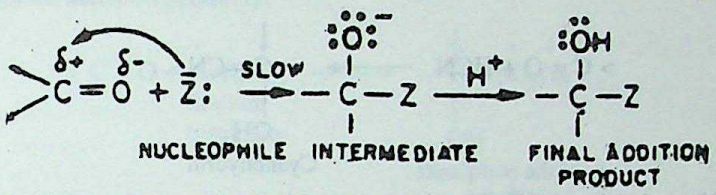
undergoes the attack of H^+ ion or other positively charged species to form the final product. The reaction in general, may be represented as :



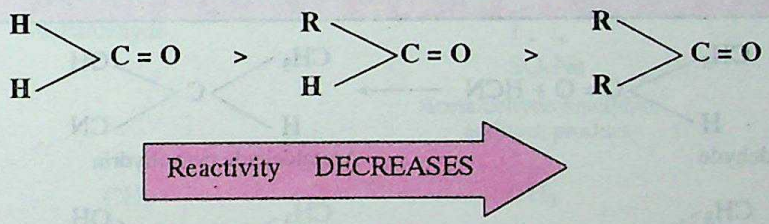
Relative Reactivity of Aldehydes and Ketones

In general, ketones are less reactive than aldehydes on account of the following facts :

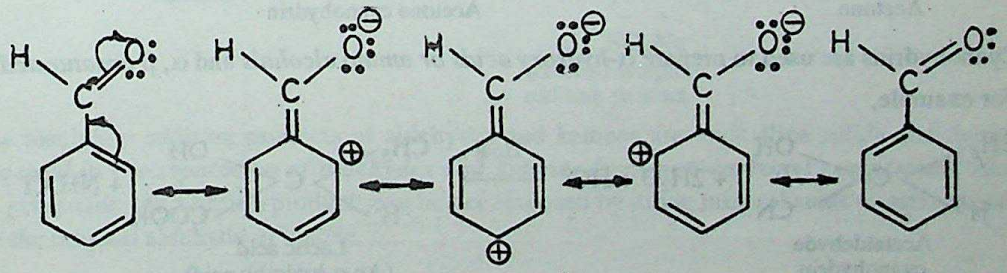
(*i*) **Electron releasing effect.** In ketones, the carbonyl carbon is attached to two alkyl groups which are *electron releasing in nature*. These alkyl groups push electrons towards carbonyl carbon and thus, decrease the magnitude of positive charge on it and make it less susceptible to nucleophilic attack.

(*ii*) **Steric effect.** In ketones, the bulk of two alkyl groups also hinders the approach of the nucleophile to the carbonyl carbon. This factor is also called steric factor.

In aldehydes, there is only one alkyl group and as a result the nucleophilic attack is relatively more easy. However, it is still easier in formaldehyde which does not contain any alkyl group. Thus, the order of reactivity is :



It may be noted that benzaldehyde is less reactive than aliphatic aldehydes. It can be explained on the basis of electron releasing resonance effect of benzene ring. The resonating structures of benzaldehyde are :



It is quite evident from the resonating structures that due to electron releasing effect (+ R effect) the magnitude of positive charge on the carbonyl group decreases and as a consequence it becomes less susceptible to the nucleophilic attack.

The reactions of aldehydes and ketones can be discussed under the following heads :

1. *Addition across C = O bond*
2. *Replacement of carbonyl oxygen by other groups*
3. *Oxidation*
4. *Reduction*
5. *Miscellaneous reactions.*

1. Addition across C = O Bond

Some of the important addition reactions are described as follows :

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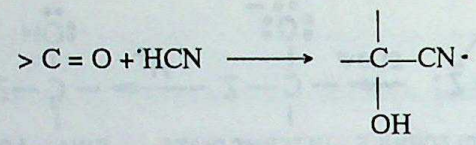
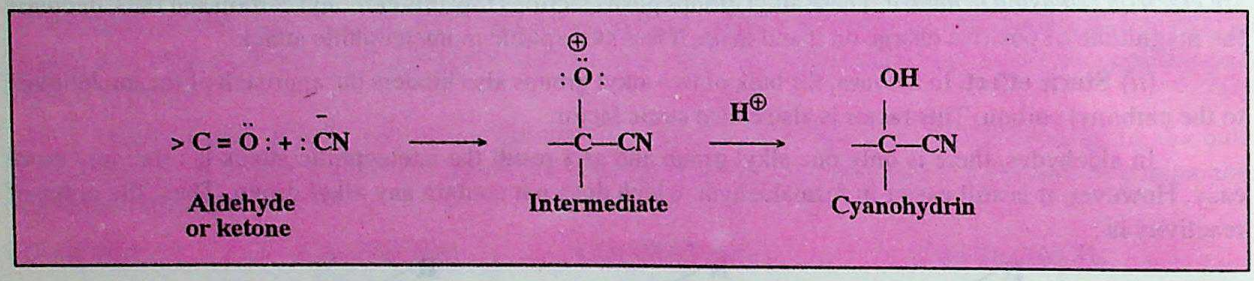
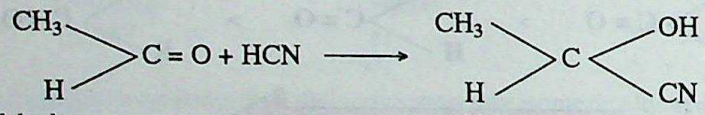
(*a*) **Addition of hydrogen cyanide.** Both aldehydes and ketones react with hydrogen cyanide (HCN) to form *cyanohydrins* as addition products. The reaction is carried out in the presence of a base which also catalyses the reaction.



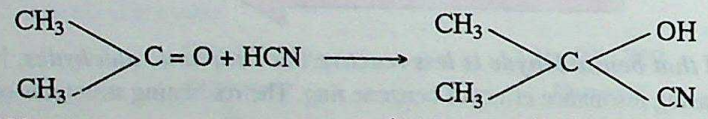
Cyanohydrin

Practically, HCN needed for the reaction is generated *in situ* by reaction of dilute HCl and NaCN. The amount of acid is generally insufficient to react with whole of NaCN. Consequently, the solution remains sufficiently alkaline (due to hydrolysis of NaCN) and catalyses the addition. The reaction is supposed to proceed by the nucleophilic attack of : $\bar{C}N$ ion as follows :



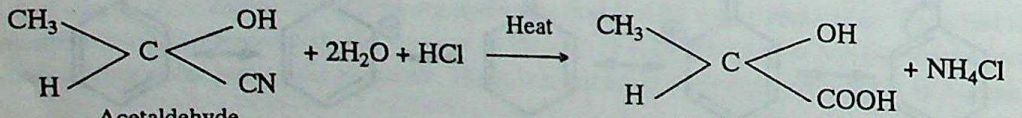


Acetaldehyde — Acetaldehyde cyanohydrin

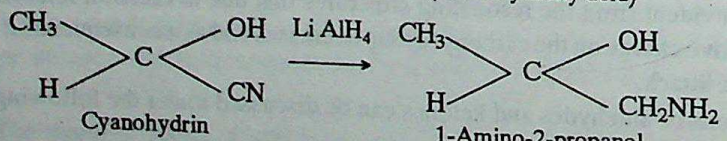


Acetone — Acetone cyanohydrin

Cyanohydrins are used to prepare α-*hydroxy acids or amino alcohols* and α, β *unsaturated acids*. For example,

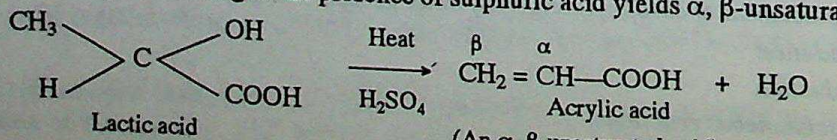


Acetaldehyde cyanohydrin — Lactic acid (An α-hydroxy acid)



Cyanohydrin — 1-Amino-2-propanol

Lactic acid on subsequent heating in the presence of sulphuric acid yields α, β-unsaturated acid.



Lactic acid — Acrylic acid (An α, β-unsaturated acid)

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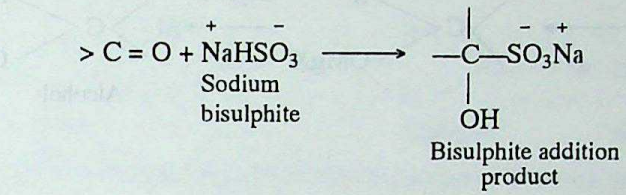
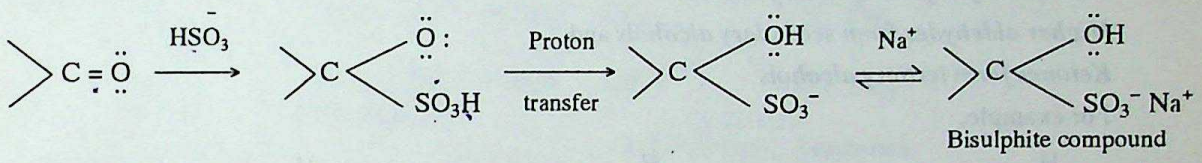
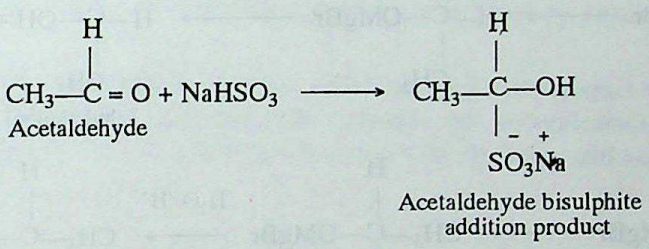
(*b*) **Addition of sodium bisulphite.** Most of the aldehydes and a few ketones like methyl ketones (ketones in which one of the alkyl group is CH_3—group) when treated with concentrated solution of sodium bisulphite, from *bisulphite addition products*.

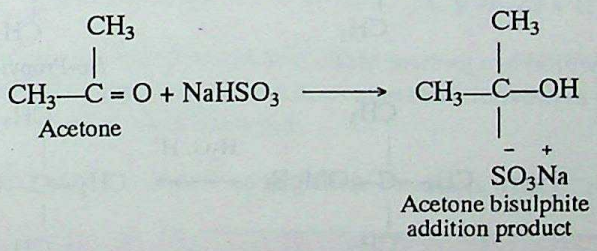


The reaction is initiated by the nucleophilic attack of bisulphite ion on the carbonyl carbon atom.

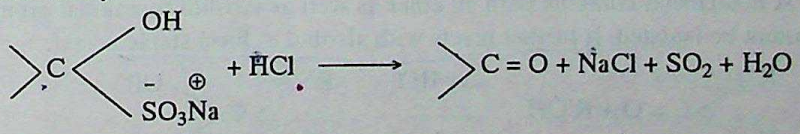


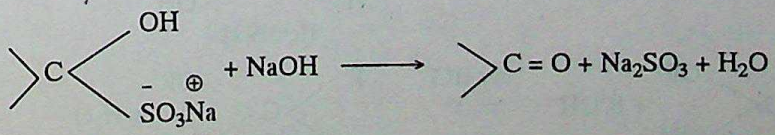
Some examples are :





The bisulphite addition products of aldehydes and ketones are crystalline solids and therefore ***this reaction is used in the separation of aldehydes and ketones from non-carbonyl compounds.*** Also as the reaction is ***reversible***, the addition products can be decomposed by dilute mineral acids or aqueous alkalies to regenerate the original aldehyde or ketone.





It may not be out of place to mention here that compounds like *diethyl ketone, benzophenone, acetophenone*, etc., do not undergo this reaction. It may presumably be due to steric hinderance of bulky groups present around the > C = O group.

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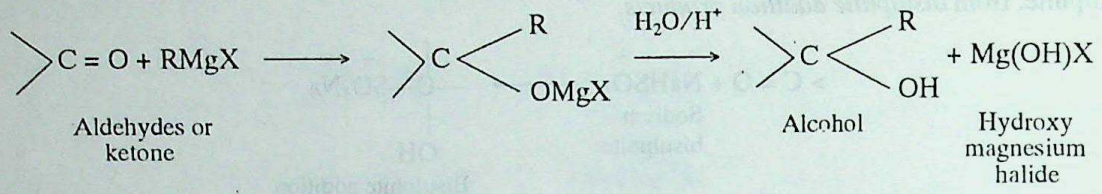
(*c*) **Addition of Grignard's Reagent.** Aldehydes and ketones react with Grignard's reagent to form addition products which on hydrolysis give alcohols.



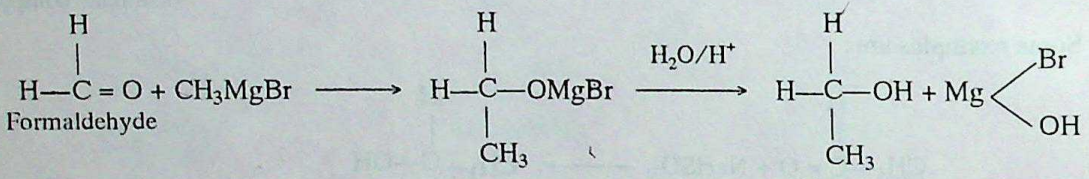
In the above reaction,

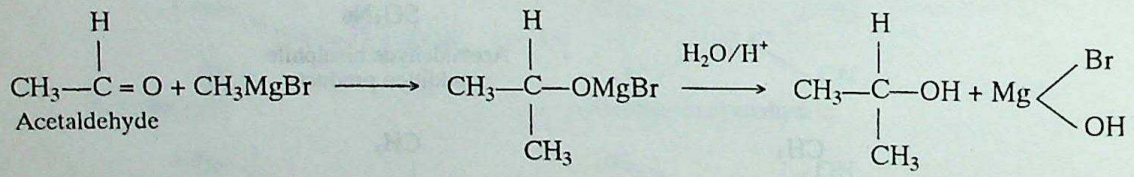
Formaldehyde forms primary alcohol

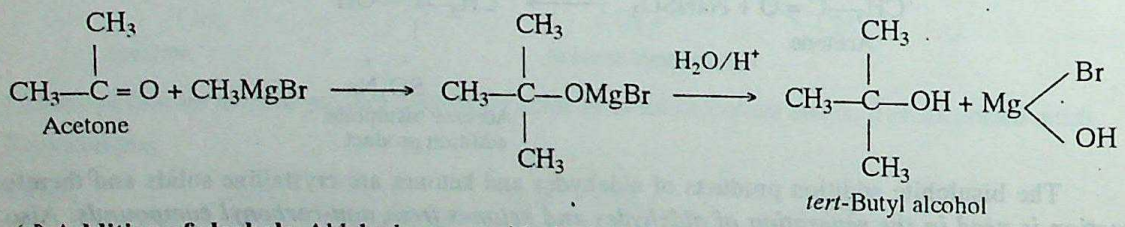
Higher aldehydes from secondary alcohols and

Ketones form tertiary alcohols

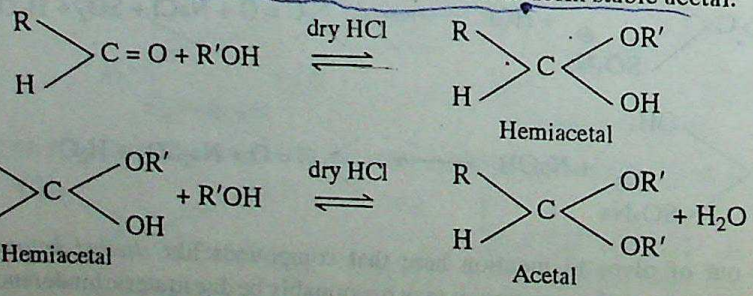
For example,







(*d*) **Addition of alcohols.** Aldehydes react with alcohols in the presence of dry HCl gas to form acetals. In this reaction, the addition of one molecule of alcohol to one molecule of aldehyde results in the formation of a **hemiacetal.** A hemiacetal contains both an ether as well as alcohol functional groups. It is an unstable compound and cannot be isolated. It further reacts with alcohol to form stable acetal.



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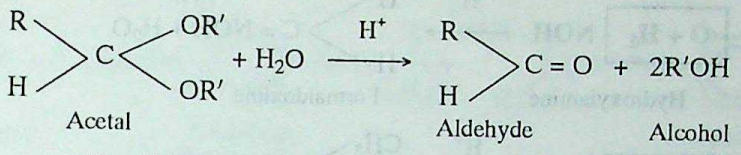
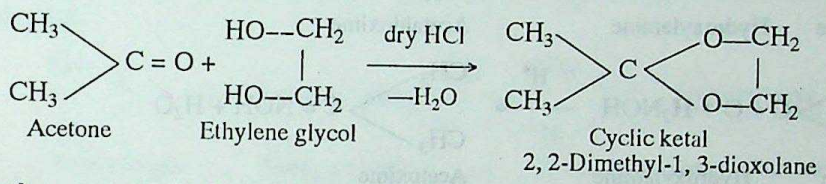
Acetals are dialkoxy compounds (geminal diethers) and have properties similar to ethers. These are quite stable to alkali but can be cleaved by acids to regenerate aldehydes. Hence acetal formation can be used to protect the aldehyde group against alkaline oxidising agents.



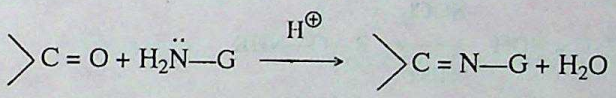
Ketones do not ordinarily react with monohydric alcohols, however, they combine with diols to give *cyclic ketals*.



2. Replacement of Carbonyl Oxygen Atom with Other Groups

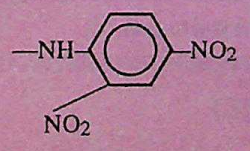
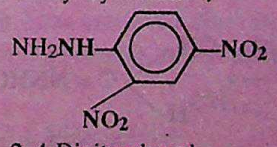
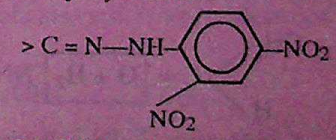
In these reactions oxygen atom of carbonyl group is replaced by either one divalent group or two monovalent groups.

(*a*) **Reaction with ammonia derivatives.** Aldehydes and ketones react with a number of ammonia derivatives such as, hydroxylamine, hydrazine, semicarbazide, etc., in weak acidic medium. In general, if we represent these derivatives by $H_2N—G$, then their reaction with aldehydes and ketones can be represented as follows :



These derivatives are crystalline solids with sharp melting and boiling points. Thus, they are used for the identification of carbonyl compounds. The various ammonia derivatives and their reaction products with carbonyl compounds are summarized in Table 8.5.

Table 8.5. Ammonia Derivatives and their Products with Carbonyl Compounds

—G	*Ammonia derivative*	*Product obtained*
—OH	NH_2OH Hydroxylamine	>C = NOH Oxime
$—NH_2$	NH_2NH_2 Hydrazine	> C = NNH_2 Hydrazone
$—NHC_6H_5$	$NH_2—NHC_6H_5$ Phenyl hydrazine	> C = $NNHC_6H_5$ Phenyl hydrazone
	 2, 4-Dinitrophenyl hydrazine	 2, 4-Dinitrophenyl hydrazone
—NHCONH$_2$	$H_2NNHCONH_2$ Semicarbazide	>C=NNHCONH$_2$ Semicarbazone

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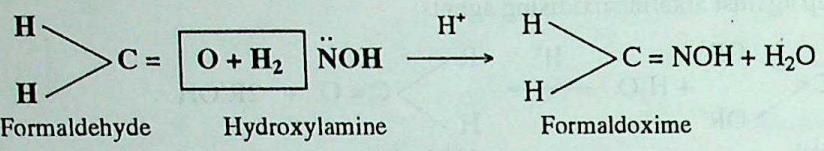
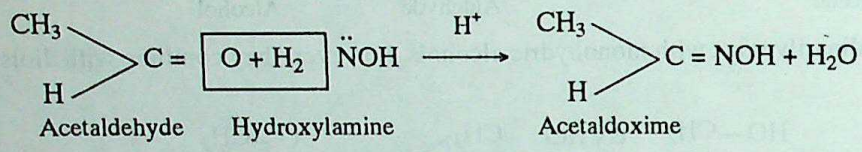
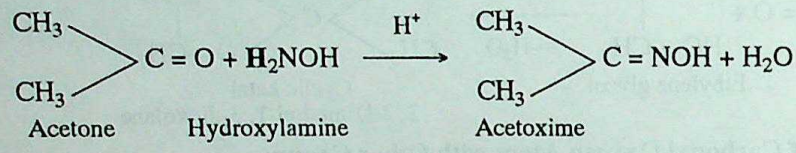
The reactions of some aldehydes and ketones with ammonia derivatives are gives below :

(*i*) **Reaction with hydroxylamine.** Aldehydes and ketones react with hydroxylamine to form **oximes.**



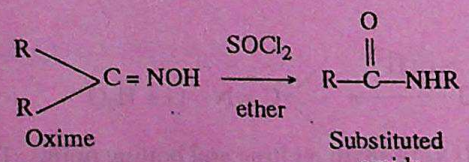




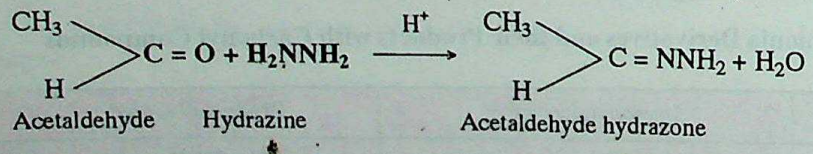
The oximes can be hydrolysed back to aldehydes and ketones by reaction with acids. These can also be reduced to amines by reaction with Na, Mg, etc.

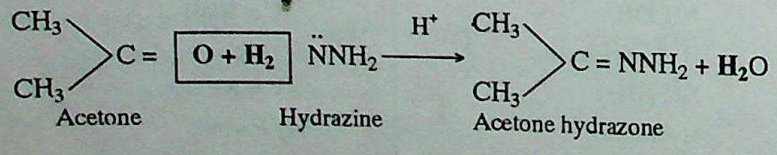
The Beckmann Rearrangement

The oximes obtained above can be transformed to amides on reaction with strong acids like H_2SO_4, $SOCl_2$, etc.

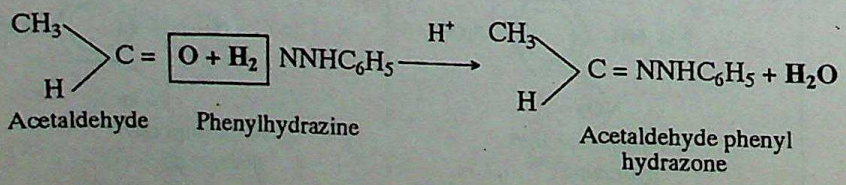


(*ii*) **Reaction with hydrazine.** Aldehydes and ketones react with hydrazine to form **hydrazones.**





(*iii*) **Reaction with phenylhydrazine.** Aldehydes and ketones react with phenylhydrazine to form **phenylhydrazones.**



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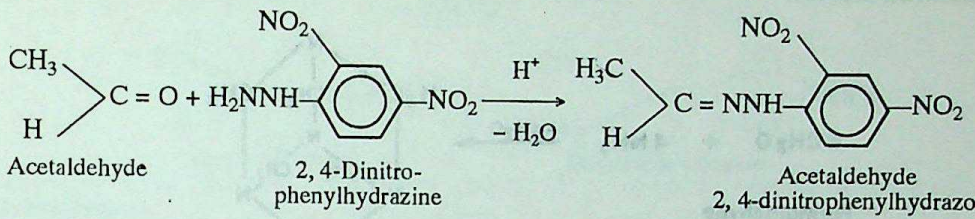
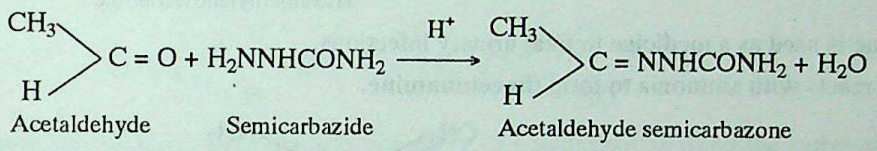
(*iv*) **Reaction with 2, 4-Dinitrophenylhydrazine.** Aldehydes and ketones react with 2, 4-dinitrophenylhydrazine to form **2, 4-dinitrophenylhydrazones** commonly known as **DNP.**

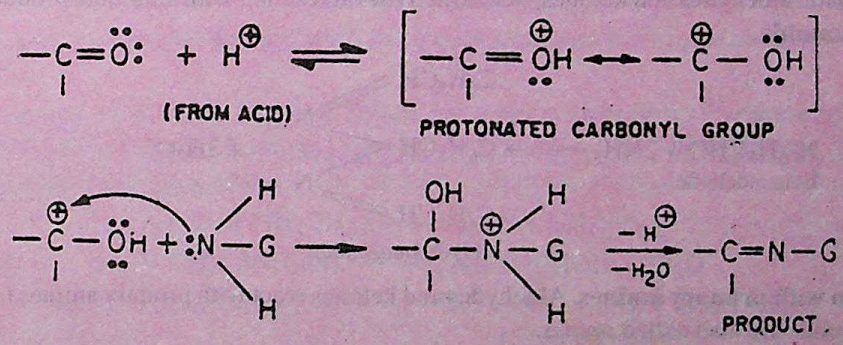


(*v*) **Reaction with semi-carbazide.** Both aldehydes and ketones react with semi-carbazide forming **semi-carbazones.**



Control of pH during reactions of ammonia derivatives

The reaction of aldehydes or ketones with ammonia derivatives is catalysed by acids. In acidic medium, the carbonyl oxygen gets protonated. Due to the presence of positive charge, the protonated carbonyl group-undergoes the nucleophilic attack of ammonia derivative very easily.

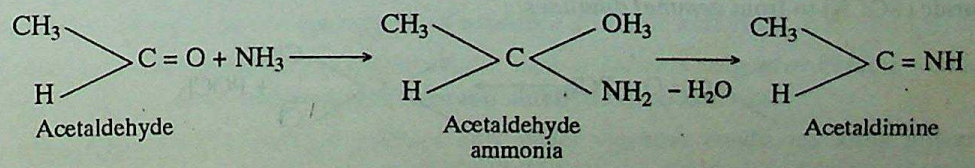


Now, if the medium is **too acidic,** then the ammonia derivatives being basic in nature form their respective salts with formula $\overset{+}{N}H_3\overset{-}{G}X$. For example in hydrochloric acid, they form respective hydrochlorides ($\overset{+}{N}H_3\overset{-}{G}Cl$). The acid salts of ammonia derivatives cannot act as nucleophiles and consequently, the reaction does not occur.

Similarly, if the medium is basic, then protonation of carbonyl group does not occur and hence, the reaction is not favoured.

Thus, for carrying out the reaction we have to properly control the pH of the medium. The optimum pH of the medium is around 3.5.

(*b*) **Reaction with ammonia.** Like ammonia derivatives, ammonia also reacts with aldehydes (except formaldehyde) and ketones to form the products, called **imines.**



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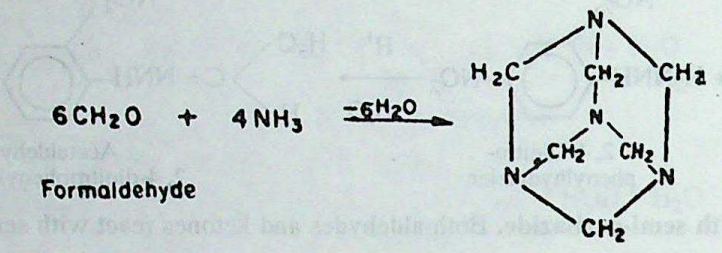
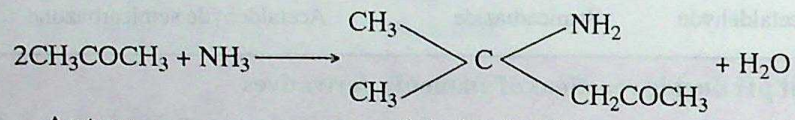
However, **formaldehyde** reacts with ammonia to form *hexamethylene tetramine,* $(CH_2)_6N_4$ also known as *urotropine* as shown below :



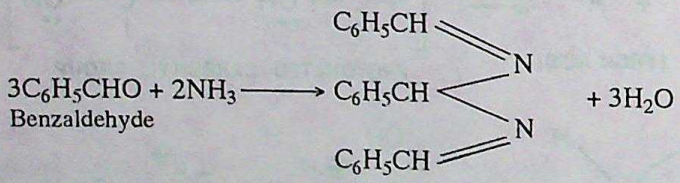
Hexamethylene tetramine

Urotropine is used as a medicine to treat urinary infections.

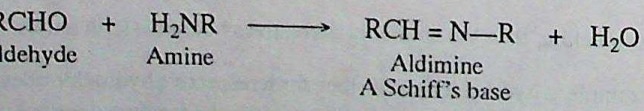
Acetone reacts with ammonia to form **diacetonamine.**

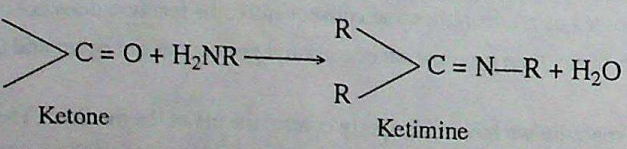


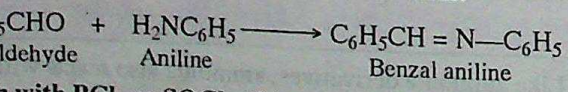
Unlike aliphatic aldehydes and ketones, **benzaldehyde** on reaction with ammonia produces a complex product, **hydrobenzamide.**



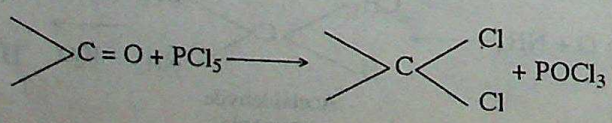
(*c*) **Reaction with primary amines.** Aldehydes and ketones react with primary amines to form *Schiff's base*. These compounds are also called *imines.*







(*d*) **Reaction with PCl_5 or $SOCl_2$ (thionyl chloride).** Aldehydes or ketones react with PCl_5 or thionyl chloride ($SOCl_2$) to from *geminal dihalides.*



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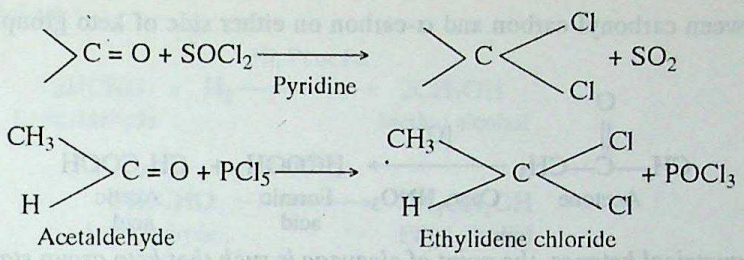
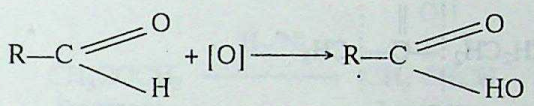


3. Oxidation

(*a*) **Oxidation of aldehydes.** Aldehydes are easily oxidised to *carboxylic acids* containing the *same number* of carbon atoms, as in parent aldehyde.



The reason for this easy oxidation is the presence of a hydrogen atom on the carbonyl carbon which can be converted into — *OH* group without involving the cleavage of any other bond. Hence, *aldehydes* are oxidised not only by *strong oxidising agents* like $KMnO_4$ and $K_2Cr_2O_7$ but also by *weak oxidising* agents like bromine water, Ag^+, Cu^{2+}, etc. As a result, aldehydes act as *strong reducing agents. They reduce* :

(*i*) *Tollen's reagent (ammoniacal $AgNO_3$) to metallic silver,*

(*ii*) *Fehling solution (alkaline $CuSO_4$ solution) to red precipitate of Cu_2O, and*

(*iii*) *Benedict's solution (alkaline $CuSO_4$ solution containing citrate ions) to red precipitate of Cu_2O as described below :*

(*i*) **Reduction of Tollen's reagent.** Tollen's reagent is ammoniacal solution of silver nitrate. On warming with this reagent, aldehydes form a silver mirror on the walls of the container. The reaction is also known as *silver mirror* test for aldehydes. The chemical reactions involved are :

$$AgNO_3 + NH_4OH \longrightarrow AgOH + NH_4NO_3$$

$$AgOH + 2NH_4OH \longrightarrow [Ag(NH_3)_2]OH + 2H_2O$$

$$\underset{\text{Aldehyde}}{RCHO} + 2[Ag(NH_3)_2]OH \longrightarrow \underset{\text{(Silver mirror)}}{RCOONH_4} + 2Ag + 3NH_3 + H_2O$$

(*ii*) **Reduction of Fehling solution.** Fehling's solution is an alkaline solution of copper sulphate containing sodium potassium tartrate (*Rochelle salt*) as the complexing agent. Aldehydes on warming with this solution, give a *red precipitate* of cuprous oxide.

$$R—CHO + 2Cu(OH)_2 + NaOH \longrightarrow RCOONa + \underset{\text{Red ppt.}}{Cu_2O} + 3H_2O$$

(*iii*) **Reduction of Bendict's solution.** Benedict's solution is alkaline copper sulphate containing citrate ions as complexing agent. Aldehydes on warming with this solution, give brick red precipitates.

$$RCHO + Cu^{2+}\text{ (complex)} \longrightarrow \underset{\text{Red ppt.}}{Cu_2O} + \underset{\text{Products}}{\text{Oxidation}}$$

It must be noted that Fehling solution and Benedict's solution are very weak oxidising agents. These can oxidise only aliphatic aldehydes but are not capable of oxidising aromatic aldehydes as benzaldehyde.

Since **ketones** *are not oxidized by weak oxidising agents, such as Tollen's reagent or Fehling solution, therefore,* **such reagents may be used to distinguish between aldehydes and ketones.**

(*b*) **Oxidation of ketones.** Ketones are oxidised only under vigorous conditions using powerful oxidising agents such as conc. HNO_3, $KMnO_4/H_2SO_4$, $K_2Cr_2O_7/H_2SO_4$, etc. Oxidation of ketones involves

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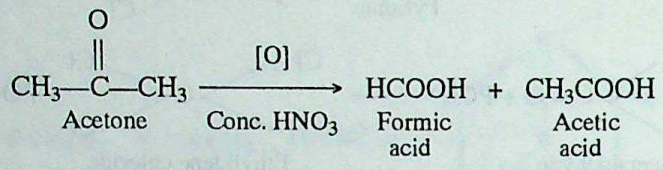
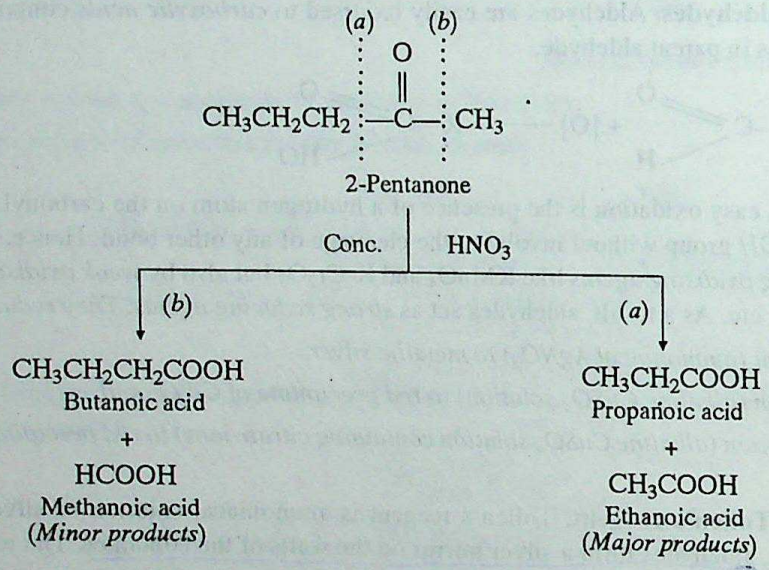
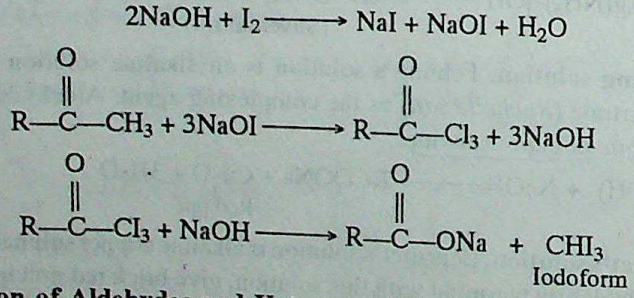
cleavage of bond between carbonyl carbon and α-carbon on either side of keto group giving a mixture of carboxylic acids.



In case unsymmetrical ketones, the point of cleavage is such that keto group stays with smaller alkyl group preferentially. This is illustrated by the example given below :

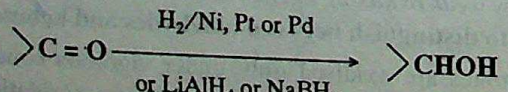


(*c*) **Oxidation with sodium hypohalite (NaOX) or (X_2 + NaOH).** This reaction is given by **acetaldehyde** or **methyl ketones** and is known as **haloform reaction.** For example, when acetaldehyde or methyl ketone is treated with *sodium hypoiodite* (I_2 + aqueous NaOH) a yellow precipitate of iodoform is obtained.



4. Reduction of Aldehydes and Ketones. Aldehydes and ketones can be reduced to a variety of compounds under different conditions and with different reducing agents.

(*a*) **Reduction to alcohols.** *Aldehydes* and *ketones* on *mild reduction* give *primary* and *secondary* alcohols respectively. This type of reduction is carried out either catalytically with H_2 in the presence of Ni, Pt or Pd or chemically by lithium aluminium hydride ($LiAlH_4$) or sodium borohydride ($NaBH_4$).



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Some examples are :

$$\underset{\text{Formaldehyde}}{2HCHO} + H_2 \xrightarrow{\text{Ni, Pt or Pd}} \underset{\text{Methyl alcohol}}{2CH_3OH}$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow{LiAlH_4} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow{LiAlH_4} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

$$\underset{\text{Propanone}}{CH_3COCH_3} \xrightarrow{H_2/Ni} \underset{\text{2-propanol}}{CH_3\overset{\overset{OH}{|}}{C}HCH_3}$$

It may be noted that lithium aluminium hydride is more powerful reducing agent then $NaBH_4$. It not only reduces aldehydes and ketones but also reduces esters, acids and nitriles as well. In contrast to this the reduction with *sodium borohydride* is so specific that it reduces only C = O bond but not C = C bond which can otherwise be reduced by the use of H_2/Ni.

$$\underset{\text{Crotonaldehyde}}{CH_3CH = CHCHO} \xrightarrow{H_2/Ni} \underset{\substack{n\text{-Butyl alcohol} \\ (\textit{Both C = C and C = O are reduced})}}{CH_3CH_2CH_2CH_2OH}$$

$$\underset{\text{Crotonaldehyde}}{CH_3CH = CHCHO} \xrightarrow{NaBH_4} \underset{\substack{\text{Crotyl alcohol} \\ (\textit{Only C = O is reduced})}}{CH_3CH = CHCH_2OH}$$

Ketones can also be reduced to secondary alcohols with aluminium isopropoxide in 2-propanol solution.

$$\underset{\text{Ketone}}{\begin{matrix} R \\ R \end{matrix}\!\!>C = O} \xrightarrow[\text{(2-Propanol)}]{[(CH_3)_2CHO]_3Al} \underset{\textit{sec}\text{-alcohol}}{\begin{matrix} R \\ R \end{matrix}\!\!>CHOH}$$

The reaction is called **Meerwein-Ponndorf** reduction.

(*b*) **Reduction to hydrocarbons.** The carbonyl group (> C = O) can be reduced to methylene (> CH_2) group resulting in the formation of alkanes by any of the following reagents :

(*i*) Zn(Hg)/HCl — ***Clemensen's reduction***

(*ii*) NH_2NH_2/KOH At 455-475 K — ***Wolff-Kishner reduction***

(*iii*) HI/P at 424 K

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Some examples of reduction reactions involving the use of above reagents are given as follows :

$$\underset{\text{Acetone}}{CH_3-\underset{\underset{O}{\|}}{C}-CH_3} + 4H \xrightarrow{Zn(Hg)/HCl} \underset{\text{Propane}}{CH_3-CH_2-CH_3} + H_2O$$

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} \xrightarrow[455-475\ K]{NH_2-NH_2/KOH} \underset{\text{Toluene}}{C_6H_5CH_3} + H_2O + N_2$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 4HI \xrightarrow[425\ K]{P} \underset{\text{Ethane}}{CH_3-CH_3} + H_2O + 2I_2$$

(*c*) **Reduction to pinacols.** Ketones on reduction with magnesium amalgam and water form **pinacols.**

$$\underset{\text{Acetone}}{CH_3-\underset{\underset{CH_3}{|}}{C}=O} + \underset{\text{Acetone}}{O=\underset{\underset{CH_3}{|}}{C}-CH_3} \xrightarrow[H_2O]{Mg-Hg} \underset{\text{2, 3-Dimethyl 2, 3-butanediol (Pinacol)}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3}$$

It is a bimolecular reduction reaction.

5. Miscellaneous Reactions

(*a*) **Reaction with Alkalies**

(*i*) **Aldol condensation.** Two molecules of an *aldehyde* or a *ketone* having **at least one α-hydrogen atom,** condense in the presence of a dilute alkali go give a β-hyroxyaldehyde or β-hydroxy-ketone. The reaction is called **aldol condensation.** ***It involves the formation of bond between carbonyl carbon of one molecule and the α-carbon atom of the other molecule.***

$$\underset{\text{Ethanal}}{CH_3-\underset{\underset{H}{|}}{\overset{\overset{O}{\|}}{C}}} + HCH_2CHO \xrightarrow{\text{Dil NaOH}} \underset{\text{Aldol (3-Hydroxybutanal)}}{\overset{4}{CH_3}-\underset{\underset{H}{|}}{\overset{\overset{OH}{|}\beta}{\overset{3}{C}}}-\overset{2}{\overset{\alpha}{C}H_2}\overset{1}{CHO}}$$

$$\underset{\text{Propanone}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{O}{\|}}{C}}} + HCH_2COCH_3 \xrightarrow{Ba(OH)_2} \underset{\text{Diacetone alcohol (4-Hydroxy-4-methyl-2-pentanone)}}{CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_2COCH_3}$$

The products of aldol condensation when heated with dilute acids undergo dehydration to form α, β-unsaturated aldehydes or ketones.

$$\underset{\text{Aldol}}{CH_3-\overset{\overset{OH}{|}}{C}H-\overset{\overset{OH}{|}}{C}H-CHO} \xrightarrow[-H_2O]{H^+,\ Heat} \underset{\text{2-Butenal}}{CH_3\overset{\beta}{C}H=\overset{\alpha}{C}HCHO}$$

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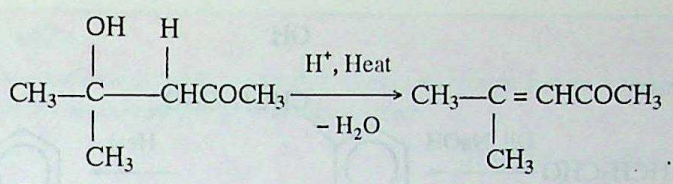
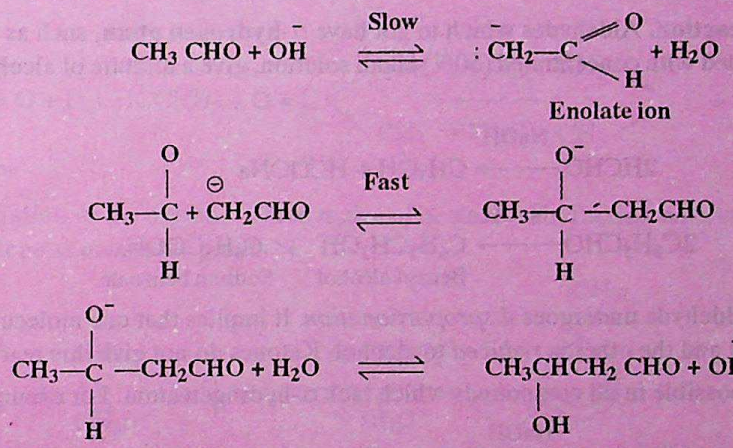


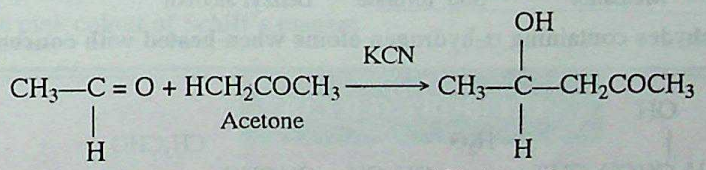
Diacetone alcohol Mesityl oxide

In general, all aldehydes and ketones which contain α-hydrogen atom can undergo this reaction. Those which do not contain α-hydrogen like HCHO, C_6H_5CHO, etc., do not undergo this reaction.

Mechanism. The formation of aldol proceeds through a series of equilibrium steps. The hydroxide ion of base abstracts the *α-hydrogen atom* from acetaldehyde and the resulting enolate ion which acts as a nucleophile attacks the second molecule of acetaldehyde. The resulting ion then takes up a proton from water to produce aldol and the $\bar{O}H$ ion is regenerated. The steps involved are :



(*ii*) **Crossed Aldol condensation.** Aldol condensation is not confined to similar molecules of aldehydes or ketones. It can also take place between different aldehydes and ketones. This type of condensation is called **crossed aldol condensation** or **mixed aldol condensation.** For example, acetaldehyde undergoes this type of condensation with acetone in the presence of KCN.



Acetaldehyde 4-Hydroxy-2-pentanone

Crossed aldol condensation can also occur between carbonyl compound having no α-H atom with aldehydes or ketones possessing α-H atom.

In this case, the carbon atom having α-H atom attaches itself to the carbonyl group of the molecule which does not have α-H atom as described in the reaction between benzaldehyde and acetaldehyde.

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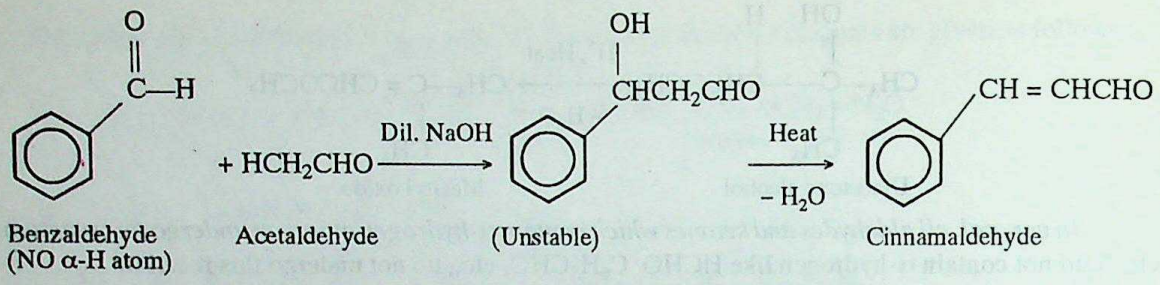

Similarly, acetone reacts with benzaldehyde in alkaline medium to form dibenzalacetone.

TEST.

$$\underset{\text{Benzaldehyde}}{2C_6H_5CHO} + \underset{\text{Acetone}}{CH_3\overset{\overset{O}{\|}}{C}CH_3} \xrightarrow{\text{Dil. NaOH}} \underset{\text{Dibenzalacetone}}{C_6H_5CH = CH\overset{\overset{O}{\|}}{C}CH = CHC_6H_5}$$

(*iii*) **Cannizzaro's reaction.** Aldehydes which to not have α-**hydrogen atom**, such as formaldehyde and benzaldehyde, when heated with concentrated (50%) alkali solution, give a mixture of alcohol and the salt of a carboxylic acid.

$$2HCHO \xrightarrow{\text{NaOH}} CH_3OH + HCOONa$$

$$2C_6H_5CHO \xrightarrow{\text{NaOH}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH} + \underset{\text{Sodium benzoate}}{C_6H_5COONa}$$

In this reaction, the aldehyde undergoes *disproportionation.* It implies that one molecule of aldehyde is *oxidised* to carboxylic acid and the other is *reduced* to alcohol. Ketones do not give this reaction.

The reaction is also possible in all compounds which lack α-hydrogen atom. For example,

$$2(CH_3)_3CCHO \xrightarrow{\text{NaOH}} (CH_3)_3CCH_2OH + (CH_3)_3CC\overset{-}{O}O\overset{+}{N}a$$

It must be noted that in *crossed Cannizaro's* reaction, when an aldehyde is treated with formaldehyde and aqueous basic solution then it is formaldehyde that undergoes oxidation.

$$\underset{\text{Benzaldehyde}}{C_6H_5CHO} + \underset{\text{Methanol}}{HCHO} \xrightarrow{\text{Base}} \underset{\text{Sod. formate}}{HC\overset{-}{O}O\overset{+}{N}a} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

On the other hand, aldehydes containing α-hydrogen atoms when heated with **concentrated alkali** give brown resinous mass.

$$2CH_3CHO \xrightarrow{\text{Alkali}} CH_3\overset{\overset{OH}{|}}{C}HCH_2CHO \xrightarrow{-H_2O} CH_3CH = CHCHO \xrightarrow{CH_3CHO}$$

$$CH_3CH = CH\underset{\underset{OH}{|}}{C}HCH_2CHO \xrightarrow{-H_2O} CH_3CH = CHCH = CHCHO$$

$$\xrightarrow{CH_3CHO} \underset{\text{Brown resinous mass}}{CH_3CH = CHCH = CH\overset{\overset{OH}{|}}{C}HCH_2CHO.....}$$

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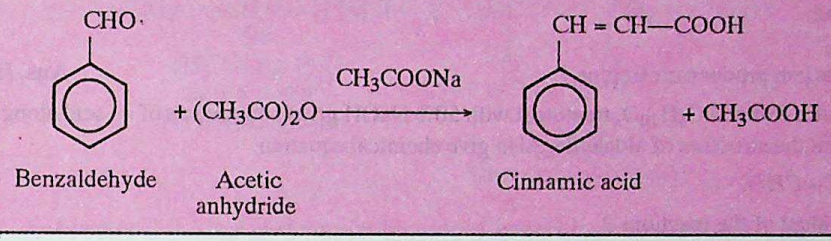
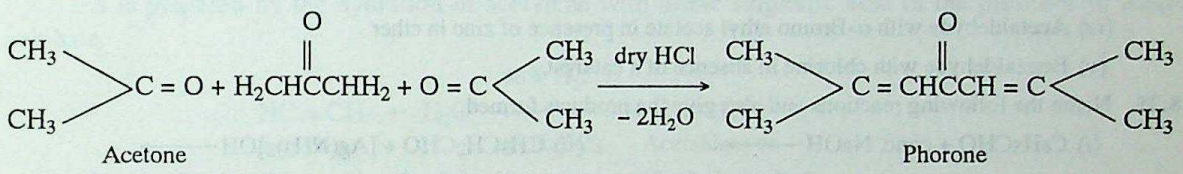
Perkin Condensation

In this reaction aromatic aldehyde is heated with an acid anhydride and its corresponding sodium salt. Acetic anhydride and sodium acetate are commonly used in this reaction.

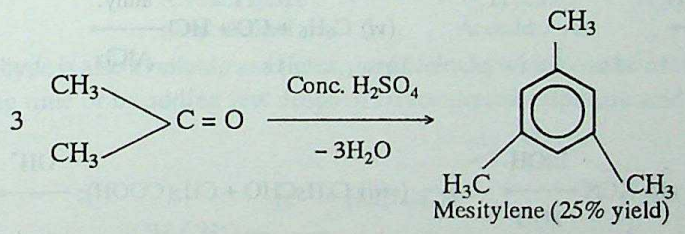


(*b*) **Reaction with Acids**

(*i*) **Formation of phorone.** Three moles of acetone condense in the presence of dry HCl to form phorone.



(*ii*) **Formation of mesitylene.** Three moles of acetone on refluxing with concentrated sulphuric acid produces mesitylene as one of the products.



TEST

(*d*) **Action with Schiff's reagent**

Schiff's reagent is an aqueous solution of magenta or pink coloured rosaniline hydrochloride* which has been decolourised by passing SO_2. When aldehydes are treated with decolourised solution of Schiff's reagent, its pink or magenta colour is restored. This reaction is used as a test for aldehydes because ketones do not restore the pink colour of Schiff's reagent.

REVIEW PROBLEMS

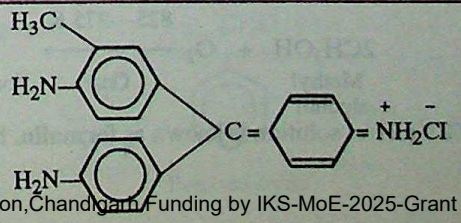
8.28. Arrange the following in order of increasing boiling points :

(A) Propanone (B) Propanal (C) Propane (D) 1-Propanol. **Ans.** $C < B < A < D$

8.29. Which reagent is used for converting propanone to 2, 3-Dimethyl-2, 3-butanediol ?

Ans. *Bimolecular reduction with (Mg-Hg)/H_2O*

*The structure of Rosaniline Hydrochloride is :



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8.30. What is the order of reactivity of the following towards HCN ?

(A) HCHO (B) $(CH_3)_2C=O$ (C) CH_3CHO. **Ans.** $A > C > B$

8.31. Which reagent can be used to separate ethanal from the mixture of ethanal, carbon tetrachloride and ethanol ? Suggest method.

Hint. $NaHSO_3$

8.32. Which reagents can produce urotropine ? **Ans.** *HCHO and* NH_3

8.33. An aldehyde with formula $C_5H_{10}O$, treatment with 50% NaOH gives sodium salt of an acid along with neopentyl alcohol, suggest the structure of aldehyde. Also give chemical equation.

Hint. $(CH_3)_3C—CHO$.

8.34. Predict the product of the reactions ?

(*i*) Butanone-2 with $LiAlH_4$

(*ii*) Acetaldehyde with Benedict's solution

(*iii*) Acetone with aniline

(*iv*) Acetaldehyde with α-Bromo ethyl acetate in presence of zinc in ether

(*v*) Benzaldehyde with chlorine in absence of a catalyst.

8.35. Name the following reactions and also give the products formed.

(*i*) $C_6H_5CHO + \text{conc. NaOH} \longrightarrow$

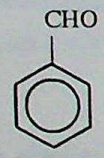
(*ii*) $CH_3CH_2CHO + [Ag(NH_3)_2]OH \longrightarrow$

(*iii*) $(CH_3)_2C=O + NH_2NH_2/KOH \longrightarrow$

(*iv*) $C_6H_5CHO + (CH_3CO)_2O \xrightarrow{CH_3COONa}$

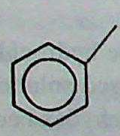
(*v*) $CH_3CHO \xrightarrow{\text{dil. NaOH}}$

(*vi*) $C_6H_6 + CO + HCl \xrightarrow[AlCl_3]{\text{anhy.}}$

(*vii*) 

$+ \text{alc. KCN} \xrightarrow[H_2O]{EtOH}$

(*viii*) $C_6H_5CHO + CH_2(COOH)_2 \xrightarrow{OH^-}$

(*ix*) 

$+ CH_3CHO \xrightarrow{OH^-}$

(*x*) $CH_3CHO \xrightarrow[\Delta]{Al(OC_2H_5)_3}$

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8.13. SOME COMMERCIALLY IMPORTANT CARBONYL COMPOUNDS

Some commercially important carbonyl compounds are *methanal, ethanal, benzaldehyde* and *propanone*. Let us discuss their industrial preparation and some uses :

1. Methanal (*Formaldehyde*) HCHO.

It is prepared by the oxidation of methyl alcohol with air in the presence of copper as catalyst.

$$\underset{\text{Methyl alcohol}}{2CH_3OH} + O_2 \xrightarrow[Cu]{825—875\ K} \underset{\text{Formaldehyde}}{2HCHO} + 2H_2O$$

Its 40% aqueous solution is known as **formalin.** It is also available as solid polymers *paraformaldehyde and trioxane*.

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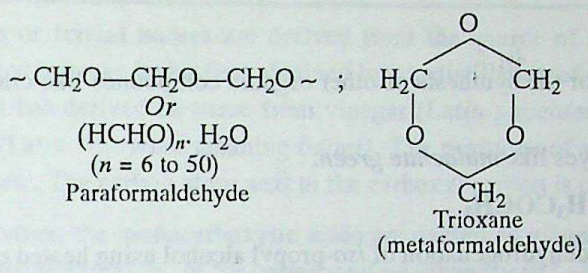
Methanal can be readily obtained from these polymers by gentle warming.



Uses. (*i*) Methanal is used in the manufacture of bakelite, resins and other polymers.

(*ii*) As formalin it is used for preserving biological samples.

2. Ethanal (*Acetaldehyde*). **CH_3CHO**

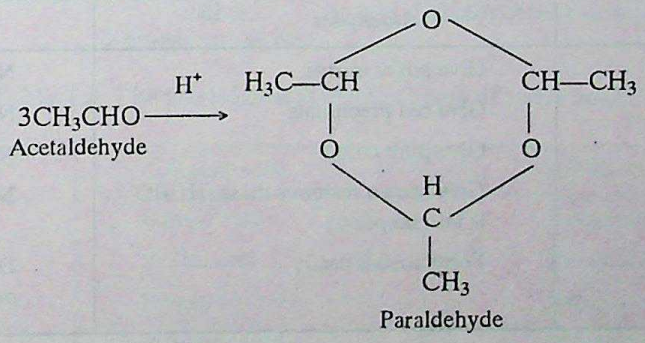
It is prepared by the hydration of acetylene with dilute sulphuric acid in the presence of mercuric sulphate.

$$\underset{\text{Acetylene}}{HC \equiv CH} + H_2O \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3CHO}$$

It may also be obtained by the dehydrogentation of ethyl alcohol.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} \xrightarrow{Cu,\ 575\ K} \underset{\text{Acetaldehyde}}{CH_3CHO} + H_2$$

Acetaldehyde is also available as a timer, *paraldehyde*, which can be obtained by allowing acetaldehyde to stand for a long time or by adding few drops of concentrated sulphuric acid to it.



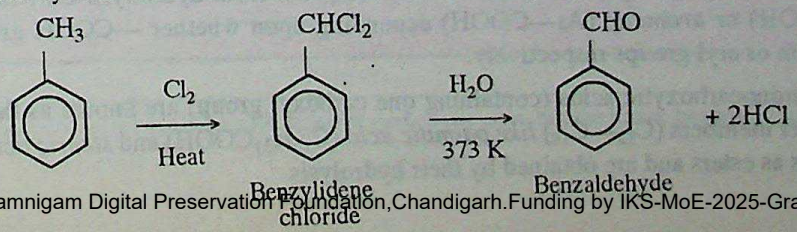
Uses. (*i*) Ethanal is used in the preparation of a number of organic compounds like acetic acid, ethyl acetate and *n*-butyl alcohol.

(*ii*) It is used in silvering of mirrors.

(*iii*) Paraldehyde is used in medicines as hypnotic.

3. Benzaldehyde

It is prepared by side chain chlorination of toluene to benzylidene chloride followed by hydrolysis.



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Uses. Benzaldehyde is used :

(*i*) In perfume industry.

(*ii*) As a starting material for the synthesis of other organic compounds like cinnamic acid, benzoyl chloride, etc.

(*iii*) In the manufacture of dyes like *malachite green.*

4. Propanone (*Acetone*). CH_3COCH_3

Acetone is prepared by the dehydrogenation of *iso*-propyl alcohol using heated copper.

$$\underset{\text{Isopropyl alcohol}}{(CH_3)_2CHOH} \xrightarrow{\text{Cu, 575 K}} \underset{\text{Acetone}}{(CH_3)_2C=O} + H_2$$

It can also be obtained by dry distillation of calcium acetate.

$$\underset{\text{Cal. acetate}}{(CH_3COO)_2Ca} \xrightarrow{\text{distillation}} CaCO_3 + \underset{\text{Acetone}}{CH_3COCH_3}$$

Uses. It is used as a solvent in the manufacture of smokeless powders (*cordite*), celluloid. It is also used as one of the ingredients of liquid nail polish.

Distinguishing Tests of Aldehydes and Ketones

Test	*Aldehydes*	*Ketones*
1. Tollen's reagent test	Give silver mirror	No silver mirror
2. Fehling solution test	Give red precipitate	No precipitate
3. Schiff's reagent test	Give pink colour	No colour
4. With NaOH	Give brown resinous mass (HCHO is an exception)	No change
5. With alcohols in presence of dry HCl	Form acetals easily	Do not from ketals easily

CARBOXYLIC ACIDS

Organic compounds containing carboxyl groups $-C\begin{matrix}=O\\-OH\end{matrix}$ possess sufficient acidic character and are called **carboxylic acids.** The carboxyl group is made up *carbonyl*, >C = O and *hydroxyl*, —OH group, hence, its name is *carboxyl group* (*carb* from carbonyl and *oxyl* from hydroxyl). Carboxylic acids may be *aliphatic* (R—COOH) or *aromatic* (Ar—COOH) depending upon whether —COOH group is attached to aliphatic alkyl chain or aryl groups respectively.

Aliphatic monocarboxylic acids (containing one carboxyl group) are known as **fatty acids** because some of their higher members (C_{12}—C_{18}) *like palmitic acid* ($C_{15}H_{31}COOH$) and *stearic acid* ($C_{17}H_{35}COOH$) exist in natural fats as esters and are obtained by their hydrolysis.

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8.14. NOMENCLATURE

The **common** or **trivial names** are derived from the source of individual acids. Formic acid, for example, was so named because it was first obtained by the distillation of ants (Latin : *fomica* meaning *ants*). Similarly, acetic acid has derived its name from vinegar (Latin : *acetum* meaning *vinegar*) Butyric acid is present in butter fat (Latin : *butyrum* meaning *butter*). The positions of substituents present is specified by Greek letters α, β, γ, etc. The carbon atom next to the carboxyl carbon is considered as α-carbon.

In **IUPAC system,** the monocarboxylic acids are named as *alkanoic acids*. The name of the acid is derived by replacing the terminal '*e*-' of the corresponding alkane with '**-oic acid**'. Carboxyl carbon is always given number one while numbering the carbon atoms of the parent chain. The position substituents are indicated by Arabic numerals.

For example,

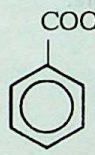
$$\overset{\delta}{\underset{5}{C}}—\overset{\gamma}{\underset{4}{C}}—\overset{\beta}{\underset{3}{C}}—\overset{\alpha}{\underset{2}{C}}—\underset{1}{COOH}$$

Common

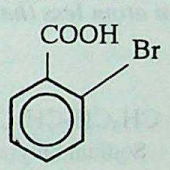
IUPAC

The trivial and IUPAC names of some mono carboxylic acids are given in Table 8.6.

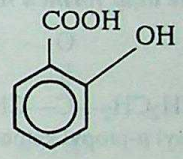
The names of aromatic acids are based on benzoic acid*. Some examples are :



Benzoic acid



o-Bromobenzoic acid or 2-Bromobenzoic acid



Salicylic acid or 2-Hydroxy benzoic acid

Table 8.6. The trivial and IUPAC names of some acids

Formula	*Common name*	*IUPAC name*
HCOOH	Formic acid	Methanoic acid
CH_3COOH	Acetic acid	Ethanoic acid
$CH_3—CH_2—COOH$	Propionic acid	Propanoic acid
$CH_3CH_2CH_2COOH$	*n*-Butyric acid	Butanoic acid
$\overset{3}{CH_3}—\overset{2}{CH}(CH_3)—\overset{1}{COOH}$	Isobutyric acid	2-Methylpropanoic acid
$CH_3CH_2CH(Br)COOH$	α-Bromobutyric acid	2-Bromobutanoic acid
$CH_3(CH_2)_3COOH$	*n*-Valeric acid	Pentanoic acid

*The systematic name of benzoic acid is *benzene carboxylic acid,* but the name, benzoic acid is more commonly used.

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8.15. GENERAL METHODS OF PREPARATION

1. By oxidation of primary alcohols. Carboxylic acids can be easily prepared by oxidation of primary alcohols with *acidified potassium permanganate* or *acidified potassium dichromate.*

$$R—CH_2OH + 2[O] \xrightarrow{KMnO_4/H^+} R—COOH + H_2O$$

$$\underset{\text{Ethyl alcohol}}{CH_3—CH_2OH} + 2[O] \xrightarrow{KMnO_4/H^+} \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

2. By oxidation of aldehydes. Aldehydes on oxidation with usual oxidizing agents give carboxylic acids with same number of carbon atoms as in the aldehyde.

$$R—CHO + [O] \longrightarrow R—COOH$$

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + [O] \longrightarrow \underset{\text{Acetic acid}}{CH_3COOH}$$

3. By oxidation of methyl ketones. Methyl ketones can also be easily oxidized to carboxylate ion by hypohalite solutions. The salts of carboxylic acid so formed, can be hydrolysed to corresponding carboxylic acid. ***In this method, the acid formed has one carbon atom less than the parent ketone.***

$$\underset{\text{Methyl } n\text{-propyl ketone}}{CH_3CH_2CH_2—\overset{\overset{O}{\|}}{C}—CH_3} \xrightarrow{NaOI} \underset{\text{Sodium butyrate}}{CH_3CH_2CH_2\overset{-}{C}OO\overset{+}{N}a} + CHI_3$$

$$CH_3CH_2CH_2\overset{-}{C}OO\overset{+}{N}a + HCl \longrightarrow CH_3CH_2CH_2COOH + NaCl$$

4. From alkyl cyanides. Alkyl cyanides on hydrolysis with dilute acids or alkalies give carboxylic acids.

$$R—CN + 2H_2O \xrightarrow{H^+} R—COOH + \overset{+}{N}H_4$$

$$\underset{\text{Methyl cyanide}}{CH_3—CN} + 2H_2O \xrightarrow{\text{dil. HCl}} \underset{\text{Acetic acid}}{CH_3COOH} + NH_4Cl$$

This method serves as a very good synthetic method for preparation of carboxylic acids.

5. By carbonation of Grignard reagents. Carboxylic acids can be obtained by carbonation of Grignard reagents. The reaction is carried out by bubbling CO_2 (dry ice is employed as source of carbondioxide) through ethereal solution of Grignard reagent and subsequent hydrolysis with dil. acids.

$$RMgX + CO_2 \longrightarrow R—\overset{\overset{O}{\|}}{C}—OMgX \xrightarrow{H_2O/H^+} R—\overset{\overset{O}{\|}}{C}—OH + Mg(OH)X$$

$$\underset{\text{Methyl mag. bromide}}{CH_3MgBr} + CO_2 \longrightarrow \left[CH_3—\overset{\overset{O}{\|}}{C}—OMgBr\right] \xrightarrow{H_2O/H^+} \underset{\text{Acetic acid}}{CH_3—\overset{\overset{O}{\|}}{C}—OH} + Mg(OH)Br$$

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This method gives carboxylic acid with one carbon more than the starting compound.

6. **From sodium alkoxide and carbon monoxide.** Heating of sodium alkoxide with CO under pressure yields sodium salt of fatty acids which on subsequent acidification gives acid.

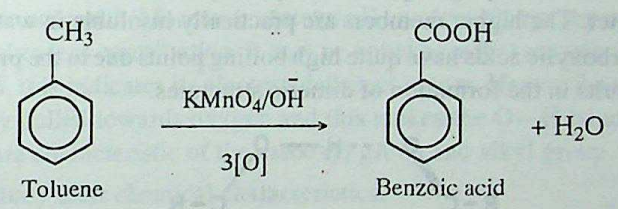
$$\underset{\text{Sodium alkoxide}}{RONa} + CO \xrightarrow[\text{Pressure}]{\text{high}} \underset{\text{Sodium salt of acid}}{RCOONa} \xrightarrow{HCl} \underset{\text{Fatty acid}}{RCOOH} + NaCl$$

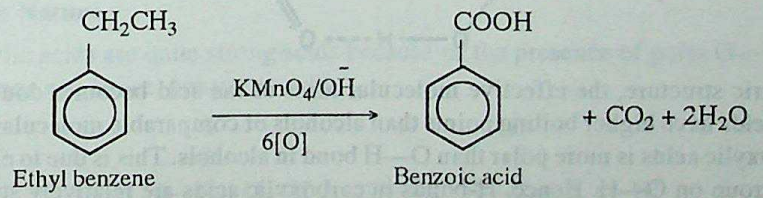
7. **From olefins.** Higher fatty acids can be obtained on large scale by heating an olefin with CO and steam under pressure at 570 K— 675 K in the presence of phosphoric acid as catalyst.

$$\underset{\text{Ethylene}}{CH_2 = CH_2} + CO + H_2O \xrightarrow[H_3PO_4]{570\text{—}675\ K} \underset{\text{Propanoic acid}}{CH_3CH_2COOH}$$

$$\underset{\text{Propene}}{CH_3CH = CH_2} + CO + H_2O \xrightarrow[H_3PO_4]{570\text{—}675\ K} \underset{\textit{iso}\text{-Butyric acid}}{(CH_3)_2CHCOOH}$$

8. **From alkyl benzenes.** Benzoic acid can be prepared by oxidation of alkyl benzenes with alkaline potassium permanganate, chromic anhydride or conc. nitric acid. The alkyl side chain gets oxidised to —COOH group irrespective of the size of the chain. Many aromatic acids are obtained industrially by this method.

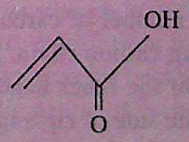


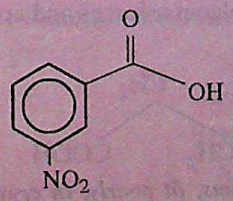


REVIEW PROBLEMS

8.36. Give IUPAC names of the following :

(*i*) $CH_3CH = CHCO_2H$

(*ii*) 

(*iii*) 

(*iv*) $(CH_3)_3C\ COOH$

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8.37. Give structures of the following :

(*i*) Phenyl acetic acid (*ii*) Iso-Valeric acid
(*iii*) Adipic acid (*iv*) Succinic acid.

8.38. Give isomers of the compound with formula $C_3H_6O_2$.

8.39. Name the kind of isomerism that can be shown by an acid with formula $C_4H_8O_2$.

8.40. How will you prepare :

(*i*) Benzoic from benzene (*ii*) Acetic acid from methyl magnesium iodide
(*iii*) Propionic acid from Ethyl bromide (*iv*) Benzoic acid from benzyl alcohol
(*v*) Phenyl acetic acid from benzene.

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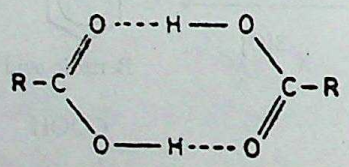
8.16. PHYSICAL PROPERTIES OF CARBOXYLIC ACIDS

1. **Physical state.** The first three aliphatic acids are colourless liquids with pungent smell. The next six are oily liquids with an odour of rancid butter while the higher members are colourless, odourless waxy solids. Benzoic acid is a crystalline solid.

2. **Solubility.** The first four aliphatic members are soluble in water due to intermolecular hydrogen bonding with water molecules.

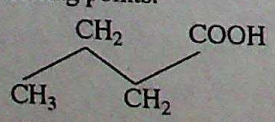
With increasing size of the alkyl group, the non-polar part of the molecule predominates thereby reducing the solubility in water. The higher members are practically insoluble in water.

3. **Boiling points.** Carboxylic acids have quite high boiling points due to the presence of intermolecular hydrogen bonding which results in the formation of dimeric structures.

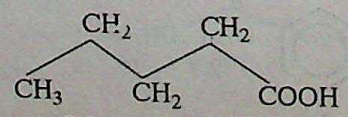


Due to dimeric structure, the effective molecular mass of the acid becomes double the actual mass. Hence, carboxylic acids have higher boiling points than alcohols of comparable molecular masses. Moreover, O—H bond in carboxylic acids is more polar than O—H bond in alcohols. This is due to electron withdrawing effect of carbonyl group on O—H. Hence, H-bonds in carboxylic acids are relatively stronger than those in alcohols.

4. **Melting points.** In first ten members of the homologous series, the **alternation effect** is observed. The alternation effect implies that the melting point of an acid with even number of carbon atoms is higher than the acid with odd number of carbon atoms above and below it. However, no such effect is observed in homologues with more than ten carbons. The alternation effect can be **explained** on the basis of the fact that in the carboxylic acids with even number of carbon atoms, the terminal methyl group and carboxylic group are on the opposite sides of zig-zag carbon chain. Hence, they fit better in the crystal lattice and it results in stronger intermolecular forces. On the other hand, acids with odd number of C atoms have carboxyl and terminal methyl groups on the same side of zig-zag carbon chain. Therefore, such molecules being relatively unsymmetrical, fit poorly in the crystal lattice. This causes weaker intermolecular forces and accounts for the relatively lower melting points.



Even no. of C-atoms, fit better, in crystal lattice, have higher m. pts. (Terminal groups are on opposite side)



Odd no. of C-atoms, fit poorly, in crystal lattice, have lower m. pts. (Terminal groups are on same side)

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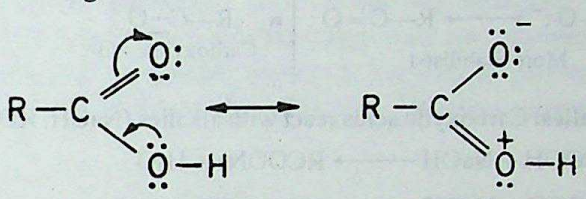
The melting and boiling points of aromatic acids are usually higher than those of aliphatic acids of comparable molecular masses. This is presumably due to the fact that planar benzene ring in these acids can pack closely in the crystal lattice than zig-zag aliphatic acids.

8.17. CHEMICAL CHARACTERISTICS OF CARBOXYLIC ACIDS

In carboxylic acids, the functional group is carboxyl group (— C(=O)—OH). Carboxylic acids are resonance hybrid of the following structures :



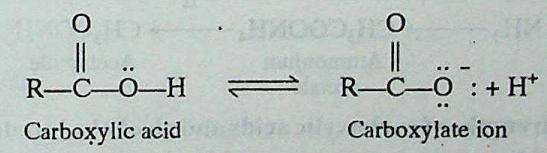
I II

From these structures, it is clear that the carbonyl part of the carboxyl group does not have a double bond character but a reduced double bond character. Thus, it does not give the reactions of the carbonyl group. Also it is evident that the two contributing structures of carboxylic acid are not equivalent, therefore, resonance stabilization in them is not much. Moreover, structure II involves charge separation, so this structure has higher energy and hence makes less contribution. It may be noted here that oxygen atom of —OH group has positive charge in structure II, this indicates its electron deficient nature. Hence, the shared pair of electrons of O—H bond will be strongly pulled towards oxygen and this makes the O—H bond quite polar. Thus, the reactions of carboxylic acids are characteristic of the carboxyl group and alkyl group.

Now, let us study their chemical characteristics.

1. **Acidic Nature**

Carboxylic acids are quite strong acids because of the presence of polar O—H group. They ionize to give hydrogen ions and hence, behave as acids.



Carboxylic acid Carboxylate ion ...(8.1)

Carboxylic acids behave as fairly strong acids. This can be explained as follows :.

Carboxylic acids as well as carboxylate ion both are stabilized by resonance. However, carboxylate ion is more stabilized by resonance because its contributing structures are exactly identical. On the other hand, the contributing structures of carboxylic acid involve charge separation. Since carboxylate ion is more stabilized by resonance than carboxylic acid, therefore, equilibrium in Eqn. (8.1) lies very much in forward direction, *i.e.*, in favour of ionized form. Hence, carboxylic acids behave as fairly strong acids. *They turn blue litmus red.* Some chemical reactions showing the acidic nature of carboxylic acids are :

(*a*) **Reaction with metals.** Carboxylic acids react with metals such as Na, K, Zn, etc., and liberate hydrogen gas.

$$2R—COOH + Zn \longrightarrow (RCOO)_2Zn + H_2$$

$$\underset{\text{Acetic acid}}{2CH_3COOH} + Zn \longrightarrow \underset{\text{Zinc acetate}}{(CH_3COO)_2Zn} + H_2$$

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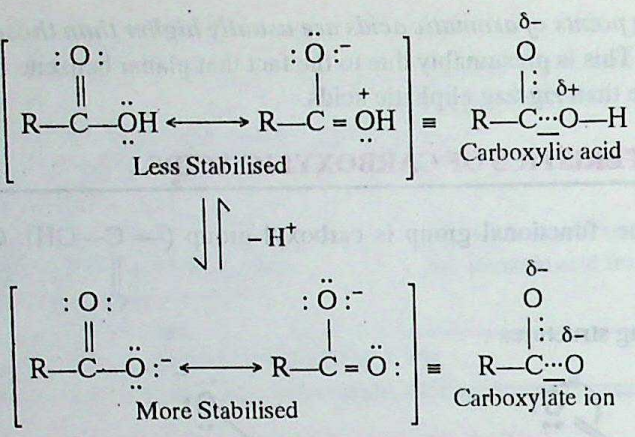


(*b*) **Reaction with alkalies.** Carboxylic acids react with alkalies (NaOH, KOH) to form salt and water.

$$RCOOH + NaOH \longrightarrow RCOONa + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NaOH \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + H_2O$$

(*c*) **Reaction with bicarbonates and carbonates.** Carboxylic acids react with bicarbonates and carbonates and produce brisk effervescence due to liberation of CO_2.

$$RCOOH + NaHCO_3 \longrightarrow RCOONa + CO_2 + H_2O$$

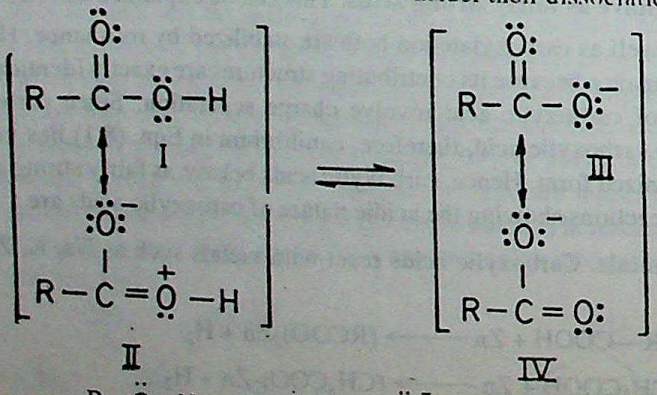
$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Sod. bicarbonate}}{NaHCO_3} \longrightarrow \underset{\text{Sod. acetate}}{CH_3COONa} + CO_2 + H_2O$$

(*d*) **Reaction with ammonia.** Carboxylic acid react with ammonia to form ammonium salts. Ammonium salts on heating give amides.

$$RCOOH + NH_3 \longrightarrow RCOO^{-}NH_4^{+} \xrightarrow{\Delta} RCONH_2 + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow{\Delta} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

Comparison of acidic strengths of carboxylic acids and alcohols. In order to understand, the relative acidic strengths of carboxylic acids and alcohols, let us consider their dissociation to give H^+ ions.



...(8.2)

$$R-\ddot{\underset{..}{O}}-H \rightleftharpoons R-\ddot{\underset{..}{O}}^{-} : + H^+ \qquad ...(8.3)$$

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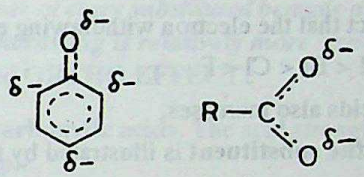
In Eqn. (8.2) though both carboxylic acid and carboxylate anion are resonance stabilised but resonance stabilization is larger in carboxylate anion than in carboxylic acid. It is because the contributing structures of carboxylate anion are identical but in carboxylic acid, the contributing structures are non-equivalent. Therefore, the equilibrium lies more towards right. On the other hand, in case of alcohols (Eqn. 8.3) neither alcohol nor alkoxide ion are stabilised by resonance and hence alcohols are weakly dissociated and behave as weaker acids than carboxylic acids.

Comparison of acid strengths of carboxylic acids and phenols

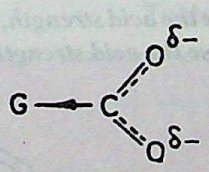
Carboxylic acids are *stronger acids* than *phenols*. It can be understood by comparing the hybrid structures of carboxylate ion and phenoxide ions. In *carboxylate ion*, the negative charge is equally distributed over two electronegative atoms (oxygen atoms) while in phenoxide ion it is present only on one oxygen. Thus, carboxylate ion is more stabilised as compared to phenoxide ion. Hence, carboxylic acids ionise to the greater extent than phenols furnishing higher concentration of H^+ ions. Therefore, carboxylic acids behave as stronger acids than phenols.



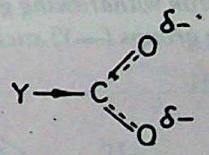
PHENOXIDE ION (LESS STABLE) CARBOXYLATE ION (MORE STABLE)

Effect of substituents on acidic strength of carboxylic acids. *The factors which increase the stability of carboxylate ion more than the carboxylic acids, increase the acidic strength of acid and the factors that decrease the stability of carboxylate ion decrease the acid strength.*

The **electron withdrawing groups** stabilize the carboxylate anion by dispersal of the negative charge and **increase** the strength of the acid. On the other hand, the **electron releasing groups** cause concentration of negative charge, destabilise the carboxylate anion and hence, decrease the strength of the acid.



Electron withdrawing group withdraws electrons, stabilizes carboxylate anion and increases acidity.



Electron donating group gives electrons, destabilizes carboxylate anion and decreases acidity.

Electron withdrawing groups such as *halo group*, —NO_2, —*CN*, etc. increase the acidity of carboxylic acids whereas electron donating groups like *alkyl groups* decrease the acidity of carboxylic acids.

The effect of various substituents on the strength of acids has been further illustrated with the help of following examples.

1. The effect of **number of the substituents** is illustrated by the chloro substituted acetic acids. The acid strength increases from chloroacetic acid to trichloroacetic acid.

$$ClCH_2COOH < Cl_2CHCOOH < Cl_3CCOOH$$

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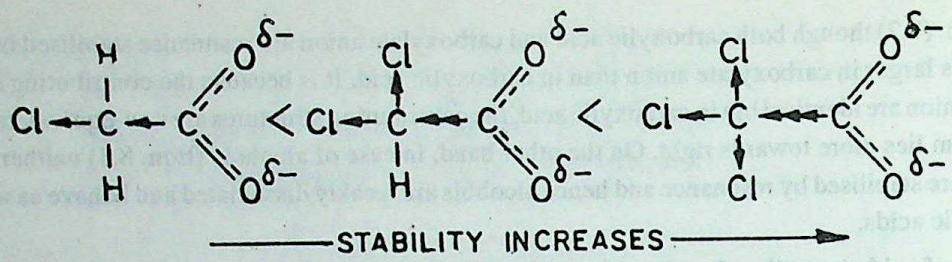


It is due to the reason that the increase in the number of chloro substituents on α-carbon atom of acetic acid makes the electron withdrawing effect more pronounced and increases the stability of corresponding conjugate base, *i.e.*, carboxylate ion.

This causes the increase in the strength of their corresponding acids.

2. The effect of **nature of the substituent** is illustrated by the various halo acetic acids. Their strength increases as

$$ICH_2COOH < BrCH_2COOH < ClCH_2COOH < FCH_2COOH$$

The above order is due to the fact that the electron withdrawing effect of halo-groups increase from

$$I < Br < Cl < F.$$

Consequently, the strength of acids also increases.

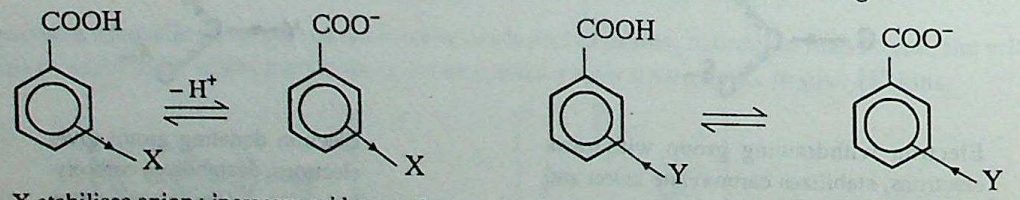
3. The effect of the **position of the substituent** is illustrated by the acidity of α-*chloro* and β-*chloro* propionic acids.

$$\overset{\alpha}{CH_3CH}(Cl)COOH \quad > \quad \overset{\beta}{CH_2}CH_2(Cl)COOH$$

The effect of the substituent decreases as its distance from the —COOH group increases. Thus, electron withdrawing effect in β-chloropropionic acid is less pronounced because —Cl group is relatively away from —COOH group. Thus, α-chloropropionic acid is stronger acid than β-chloropropionic acid.

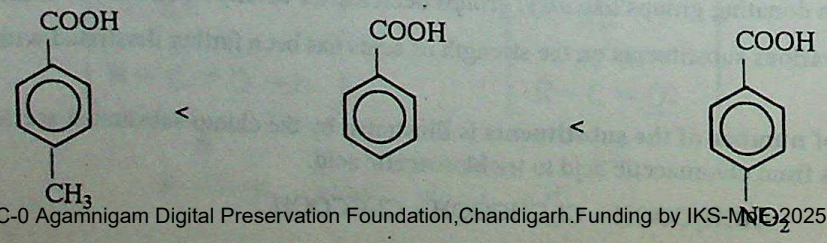
Acid strength of subsituted benzoic acids

(*i*) ***The electron withdrawing groups like —Cl, —NO_2, increase the acid strength, whereas electron releasing groups (—Y) such as —CH_3, —NH_2, etc., decrease the acid strength.***



X stabilises anion ; increases acid strength Y destabilises anion ; decreases acid strength

For example, *p*-toluic acid is less stronger than phenol while *p*-nitrobenzoic acid is more stronger than benzoic aicd



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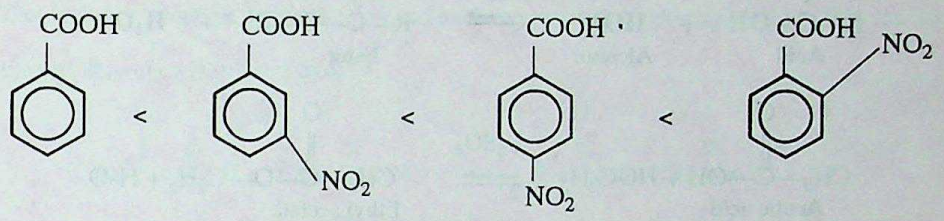
Acid strength INCREASES

(*iii*) ***The effect is more pronounced at para position as compared to that at meta position.*** For example,



Acid strength INCREASES

(*iv*) ***The ortho subsituted isomer of every substituted benzoic acid (whether the substituent is electron releasing or electron withdrawing is relatively more stronger than the corresponding para*** and ***meta*** isomer. This is called **ORTHO EFFECT.**

Measurement of acidity of carboxylic acids. The acid strength of carboxylic acids is measured from their dissociation constant. For example,

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$K_a = \frac{[RCOO^-][H_3O^+]}{[RCOOH]}$$

where K_a is the dissociation constant of acid. Higher the value of K_a stronger the acid will be. As the numerical values of K_a vary by large magnitude, therefore, it is more convenient to express the acidic strength in terms of its pK_a value ($= -\log K_a$). Now, *smaller is the value of pK_a, stronger is the acid and vice versa.* The K_a and pK_a values of some acids are given in Table 8.7.

Table 8.7. K_a and pk_a Values of some Acids

Acid	K_a	pK_a
HCOOH	1.77×10^{-4}	3.75
CH_3COOH	1.8×10^{-5}	4.74
FCH_2COOH	2.6×10^{-3}	2.59
$ClCH_2COOH$	1.4×10^{-3}	2.86
$BrCH_2COOH$	1.3×10^{-3}	2.90
ICH_2COOH	6.7×10^{-4}	3.18
$Cl_2CHCOOH$	5.5×10^{-2}	1.26
Cl_3CCOOH	2.3×10^{-1}	0.64
CH_3CH_2COOH	1.3×10^{-5}	4.87
C_6H_5COOH	6.3×10^{-5}	4.20
$C_6H_5CH_2COOH$	4.9×10^{-5}	4.31
$HOCH_2COOH$	1.5×10^{-4}	3.83

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2. Reactions involving replacement of —OH group

(*a*) **Esterification.** Carboxylic acids react with alcohols in the presence of conc. H_2SO_4 to form esters.

$$\underset{\text{Acid}}{R-\overset{\overset{O}{\|}}{C}-OH} + \underset{\text{Alcohol}}{HOR'} \overset{H^+}{\rightleftharpoons} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-O-R'} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3-\overset{\overset{O}{\|}}{C}-OH} + HOC_2H_5 \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{Ethyl acetate}}{CH_3-\overset{\overset{O}{\|}}{C}-O-C_2H_5} + H_2O$$

This reaction is reversible. In order to shift the equilibrium in forward direction water is removed as soon as it is formed.

(*b*) **Formation of acid amides.** On treatment with ammonia, ammonium salts are formed which upon heating result in the formation of acid amides.

$$\underset{\text{Acid}}{RCOOH} + NH_3 \longrightarrow \underset{\text{Amm. salts}}{RCOONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acid amide}}{RCONH_2} + H_2O$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + NH_3 \longrightarrow \underset{\text{Amm. acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

(*c*) **Formation of acid chlorides.** Carboxylic acids react with PCl_5 or $SOCl_2$ (thionyl chloride) in pyridine to form acid chlorides.

$$\underset{\text{Acid}}{RCOOH} + PCl_5 \xrightarrow{C_5H_5N} \underset{\text{Acid chloride}}{RCOCl} + POCl_3 + HCl$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + PCl_5 \xrightarrow{C_5H_5N} \underset{\text{Acetyl chloride}}{CH_3COCl} + POCl_3 + HCl$$

$$\underset{\text{Acid}}{RCOOH} + SOCl_2 \xrightarrow{C_5H_5N} \underset{\text{Acid chloride}}{RCOCl} + SO_2 + HCl$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + SOCl_2 \xrightarrow{C_5H_5N} \underset{\text{Acetyl chloride}}{CH_3COCl} + SO_2 + HCl$$

(*d*) **Formation of acid anhydrides.** Carboxylic acids on treatment with phosphorus pentoxide form anhydrides by elimination of a water molecule from two molecules of the carboxylic acid as :

$$R-\overset{\overset{O}{\|}}{C}-OH + H-O-\overset{\overset{O}{\|}}{C}-R \xrightarrow{P_2O_5} \underset{\text{Acid anhydride}}{R-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-R} + H_2O$$

$$CH_3-\overset{\overset{O}{\|}}{C}-OH + H-O-\overset{\overset{O}{\|}}{C}-CH_3 \xrightarrow{P_2O_5} \underset{\text{Acetic anhydride}}{CH_3-\overset{\overset{O}{\|}}{C}-O-\overset{\overset{O}{\|}}{C}-CH_3} + H_2O$$

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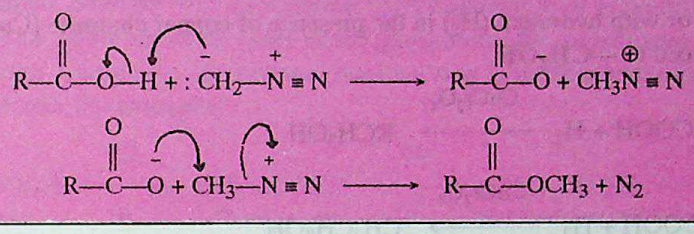
Formation of esters by reaction with diazomethane

Carboxylic acids on reaction with diazomethane produce *methyl esters* as the product.

$$RCOOH + CH_2N_2 \longrightarrow RCOOCH_3 + N_2$$

Mechanism

The acid first transfers its proton to diazomethane producing carboxylate ion. This ion then attacks as a nucleophile on $CH_3-\overset{+}{N}\equiv N$ to yield an ester.



3. Reactions involving complete—COOH group

(*a*) **Soda lime decarboxylation.** Sodium or potassium salts of carboxylic acids on heating with soda-lime (NaOH and CaO) give *alkanes with one carbon less than the parent acids*. In this reaction while NaOH takes part in the reaction, CaO simply helps in fusion of NaOH.

$$\underset{\text{Sodium salt of acid}}{RCOONa} + NaOH \xrightarrow{CaO} \underset{\text{Alkane}}{R-H} + Na_2CO_3$$

$$\underset{\text{Sod. acetate}}{CH_3COONa} + NaOH \xrightarrow{CaO} \underset{\text{Methane}}{CH_4} + Na_2CO_3$$

The reaction can be employed for descending down the series i.e., decreasing one carbon in a chain.

(*b*) **Kolbe's electrolytic decarboxylation.** The aqueous solutions of sodium or potassium salts of carboxylic acids on electrolysis give alkanes at anode. This reaction is called Kolbe's electrolysis.

$$RCOONa\ (aq) \longrightarrow RCOO^- + Na^+$$

At anode : $2RCOO^- \longrightarrow \underset{\text{Alkane}}{R-R} + 2CO_2 + 2e^-$

At cathode : $2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$

(*c*) **Dry distillation of calcium salts of carboxylic acids.** Calcium salts of carboxylic acids on heating give aldehydes or ketones.

(*i*) *When calcium formate is distilled, formaldehyde is formed.*

$$\underset{\text{Calcium formate}}{\begin{matrix} HCOO \\ HCOO \end{matrix}\!\!>Ca} \xrightarrow{\Delta} CaCO_3 + \underset{\text{Formaldehyde}}{HCHO}$$

(*ii*) *When calcium formate is distilled with calcium acetate, acetaldehyde is formed.*

$$\underset{\text{Calcium formate}}{\begin{matrix} HCOO \\ HCOO \end{matrix}\!\!>Ca} + \underset{\text{Calcium acetate}}{Ca\begin{matrix} OOCCH_3 \\ OOCCH_3 \end{matrix}} \xrightarrow{\Delta} 2CaCO_3 + \underset{\text{Acetaldehyde}}{CH_3CHO}$$

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(*iii*) *When calcium acetate is distilled alone, acetone is formed.*

$$\underset{\text{Calcium acetate}}{\begin{matrix} CH_3COO \\ CH_3COO \end{matrix}\!\!>Ca} \xrightarrow{\text{Distill}} CaCO_3 + \underset{\text{Acetone}}{CH_3\overset{\overset{O}{\|}}{C}CH_3}$$

(*d*) **Reduction.** (*i*) *Partial reduction.* Carboxylic acids are reduced to primary alcohols with lithium aluminium hydride ($LiAlH_4$), or with hydrogen (H_2) in the presence of copper chromite ($CuCr_2O_4$) catalyst. Here, —**COOH** group is reduced to —$\mathbf{CH_2OH}$.

$$RCOOH + H_2 \xrightarrow{CuCr_2O_4} RCH_2OH$$

$$CH_3COOH + H_2 \xrightarrow{CuCr_2O_4} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

$$\underset{\text{Ethanoic acid}}{CH_3COOH} + 4H \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} + H_2O$$

The reduction of acids, however, does not take place with $NaBH_4$.

(*ii*) *Complete reduction.* Carboxylic acids are reduced to alkanes on reaction with HI in the presence of phosphorus at about 500 K. Here, —*COOH* group is reduced to —CH_3.

$$\underset{\text{Acid}}{RCOOH} + 6HI \xrightarrow[500\ K]{P} \underset{\text{Alkane}}{RCH_3} + 3H_2O + 3I_2$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + 6HI \xrightarrow[500\ K]{P} \underset{\text{Ethane}}{CH_3CH_3} + 2H_2O + 3I_2$$

(*e*) **Hunsdiecker reaction.** Silver salts of carboxylic acids on treatment with Br_2 in the presence of some inert solvent such as CCl_4 give alkyl bromides with one carbon atom less than the parent acids.

$$RCOOAg + Br_2 \xrightarrow{CCl_4} RBr + CO_2\uparrow + AgBr$$

$$\underset{\text{Silver acetate}}{CH_3COOAg} + Br_2 \xrightarrow{CCl_4} \underset{\text{Methyl bromide}}{CH_3Br} + CO_2\uparrow + AgBr$$

4. Reaction involving alkyl group of carboxylic acids

(*a*) **Oxidation.** When acids are treated with mild oxidising agents such as H_2O_2, the alkyl group is oxidised at the β-position. For example :

$$\underset{n\text{-Butyric acid}}{CH_3\overset{\beta}{C}H_2\overset{\alpha}{C}H_2COOH} \xrightarrow[H_2O_2]{[O]} \underset{\beta\text{-Hydroxy butyric acid}}{CH_3\overset{\overset{OH}{|}}{C}HCH_2COOH}$$

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Carboxylic acids can also be oxidised at α-carbon by oxidising agents like selenium dioxide, SeO_2. Keto acids are obtained as product in this reaction.

$$\underset{\text{Carboxylic acid}}{RCH_2COOH} \xrightarrow[\text{Heat}]{SeO_2} \underset{\alpha\text{-keto acid}}{R-\overset{\overset{O}{\|}}{C}-COOH} + H_2O + Se$$

(*b*) **Hell Volhard Zelinsky (HVZ) reaction** (*α-Halogenation of aliphatic acids*). When carboxylic acids are treated with Cl_2 or Br_2 in the presence of red phosphorus, the α-hydrogen atoms of carboxylic acids are replaced by chlorine or bromine. The reaction does not stop at monosubstitution but continues till all the α-hydrogens are replaced. For example :

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[P]{Cl_2} \underset{\text{Chloroacetic acid}}{CH_2ClCOOH} \xrightarrow[P]{Cl_2} \underset{\text{Dichloroacetic acid}}{CHCl_2COOH} \xrightarrow[P]{Cl_2} \underset{\text{Trichloracetic acid}}{CCl_3COOH}$$

Function of red phosphorus. Its function is to convert carboxylic acid to an acid halide, which being more reactive than the parent acid undergoes α-halogenation easily.

$$2P + 3Br_2 \longrightarrow 2PBr_3$$

$$3CH_3CH_2COOH + PBr_3 \longrightarrow \underset{\text{Propionyl bromide}}{3CH_3CH_2COBr} + H_3PO_3$$

$$CH_3CH_2-\overset{\overset{O}{\|}}{C}-Br + Br_2 \xrightarrow{-HBr} CH_3\underset{\underset{Br}{|}}{CH}-\underset{\underset{O}{\|}}{C}-Br$$

$$CH_3-\underset{\underset{Br}{|}}{CH}-\underset{\underset{O}{\|}}{C}-Br + CH_3CH_2COOH \longrightarrow CH_3\underset{\underset{Br}{|}}{CH}-COOH + CH_3CH_2-\overset{\overset{O}{\|}}{C}Br$$

The propionyl bromide produced then reacts again and again till the whole of acid is converted to α-substituted acid.

The reaction has a great synthetic importance as the halogen atom can be replaced by a number of other groups giving useful products. Some examples are :

$$\underset{\alpha\text{-chloroacid}}{RCH_2\underset{\underset{Cl}{|}}{CH}COOH} \xrightarrow[-HCl]{NH_3} \underset{\alpha\text{-Amino acid}}{RCH_2\underset{\underset{NH_2}{|}}{CH}COOH}$$

$$\xrightarrow[-KCl]{KOH(aq)} \underset{\alpha\text{-Hydroxy acid}}{RCH_2\underset{\underset{OH}{|}}{CH}COOH}$$

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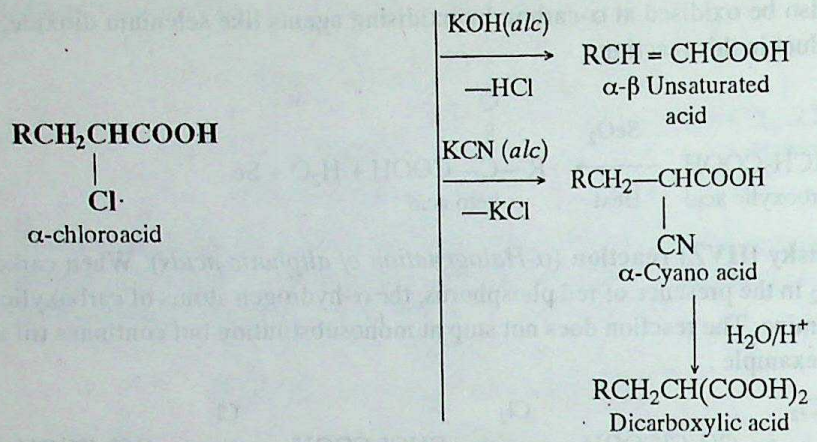
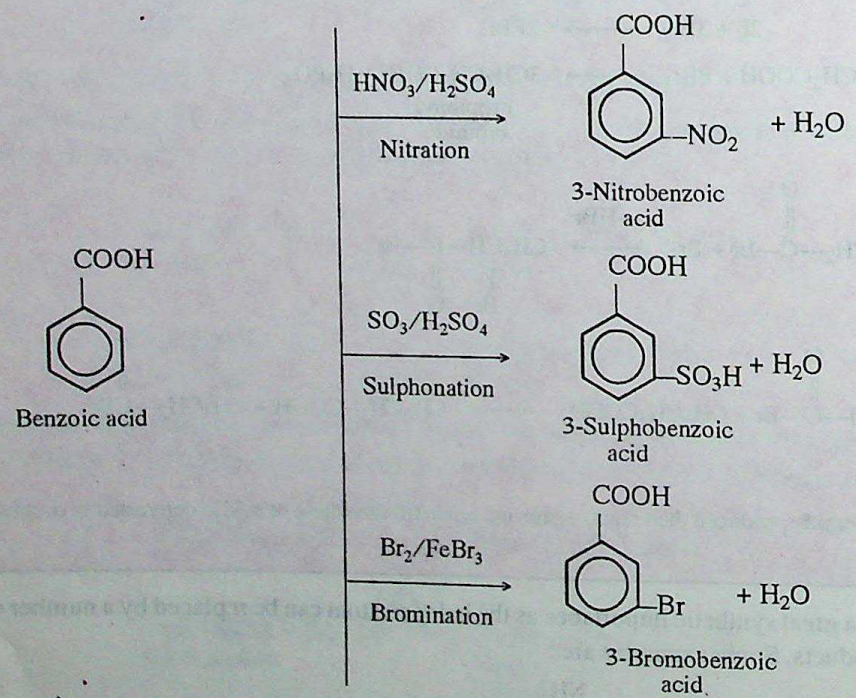


Ring Substitution Reactions in Benzoic Acid

Carboxyl group is *electron withdrawing group*. It decreases the electron density at benzene ring and hence, deactivates it towards electrophilic substitution reactions. Substitution in benzoic acid takes place mainly at *meta* position. Some examples are given below :



REVIEW PROBLEMS

8.41. Which bond C—OH or CO—H of carboxylic acids is broken when :

(*i*) Acid chloride is formed (*ii*) Acid reacts with alcohol

(*iii*) Acid reacts with Na.

Ans. (*i*) *C—OH* (*ii*) *C—OH* (*iii*) *CO—H*

8.42. Which acid is formed when *p*-bromotoluene is oxidised ?

Ans. *4-bromobenzoic acid*

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8.43. Give the IUPAC name of potassium α, β-dibromo iso-butyrate.

Hint. *The structure is* $CH_2(Br)—C(CH_3)(Br)—COOK$ *Potassium-2, 3-dibromo-2-methylpropanoate.*

8.44. Which out of α-nitro butyric acid and β-nitro butyric acid is a more stronger acid ? **Ans.** *α-nitrobutyric acid*

8.45. Which halide is formed when silver iso-butyrate is treated with Br_2 in CCl_4. Give equation.

Ans. *2-bromopropane*

8.46. Suggest method to prepare benzoic acid from acetophenone. Give equation.

Hint. *Acetophenone* $\xrightarrow[(ii)\ H_2O/H^+]{(i)\ NaOI}$ *Benzoic Acid*

8.47. The common names of some acids are given below. Write their systematic IUPAC names.

(*i*) $C_6H_5—CH(OH)CO_2H$ (mendelic acid) (*ii*) $CH_2 = C(CH_3)CO_2H$ (methacrylic acid)

(*iii*) $(CH_3)_3CCO_2H$ (pivalic acid) (*iv*) $CH_3COCOOH$ (pyruvic acid).

Ans. (*i*) *2-Hydroxy-2-phenylethanoic acid*
(*ii*) *2-Methyl prop-2-enoic acid*
(*iii*) *2, 2-Dimethyl propanoic acid*
(*iv*) *2-Ketopropanoic acid*

8.48. How will you prepare

(*i*) Ethanoic acid from propanone (*ii*) *m*-nitro benzoic acid from benzene

(*iii*) Ethyl acetate from acetic acid (*iv*) Chloroacetic acid from acetic acid

(*v*) Acetic acid from methyl bromide.

8.49. Which of the following is a stronger acid in each of the following pairs ?

(*i*) monochloro, dichloro and trichloro acetic acid

(*ii*) α-chloropropionic acid and β-fluoro propionic acid

(*iii*) propionic acid, acetic and formic acid

(*iv*) *m*-hydroxy benzoic acid and *p*-hydroxy benzoic acid

(*v*) Acetic acid and benzoic acid.

8.50. Convert acetic acid to the following in one step :

(*i*) Methanol (*ii*) Malonic acid.

8.51. What is pyruvic acid ? Which optically active acid is obtained from it.

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8.18. SOME COMMERCIALLY IMPORTANT CARBOXYLIC ACIDS

Some commercially important carboxylic acids are *methanoic acid, ethanoic acid* and *benzoic acid.* Let us study their industrial preparation and uses.

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1. **Methanoic acid** (*formic acid*). It is prepared on large scale by reacting carbon monoxide with aqueous sodium hydroxide under the pressure of 1 atmosphere and 473 K.

$$CO + NaOH \xrightarrow[\text{1 atm.}]{\text{473 K}} \underset{\text{Sodium formate}}{HCOONa}$$

$$HCOONa \xrightarrow{H_2O/H^+} \underset{\text{Formic acid}}{HCOOH}$$

Methanoic acid is used in *rubber, leather* and *electroplating industry*.

2. Ethanoic acid (*acetic acid*)

(*i*) *From acetylene*. Acetylene is first oxidized with 40%, H_2SO_4 in the presence of mercuric sulphate.

$$\underset{\text{Acetylene}}{H—C \equiv C—H} + H_2O \xrightarrow[\text{1\% } HgSO_4]{\text{40\% } H_2SO_4} \underset{\text{Acetaldehyde}}{CH_3—CHO}$$

Acetaldehyde is finally oxidised to acid with air in the presence of manganous acetate catalyst.

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + [O] \xrightarrow[\text{Acetate}]{\text{Manganous}} \underset{\text{Acetic acid}}{CH_3COOH}$$

(*ii*) *From ethyl alcohol*. In this method, ethyl alcohol is first dehydrogenated with hot reduced copper to acetaldehyde. The acetaldehyde obtained is oxidized with air in the presence of manganous acetate as catalyst to acetic acid.

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} \xrightarrow[-H_2]{\text{Cu/575 K}} \underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[\text{Manganous acetate}]{+[O]} \underset{\text{Aectic acid}}{CH_3COOH}$$

It can also be produced from carboxylation of methanol in the presence of *rhodium* catalyst.

$$CH_3OH + CO \xrightarrow{Rh} CH_3COOH$$

Acetic acid is also obtained in dilute form (called *vinegar*) by the fermentation of ethyl alcohol with bacteria, *acetobacter* in the presence of air. This is a very old method for obtaining vinegar.

$$\underset{\text{Ethyl alcohol}}{CH_3CH_2OH} + O_2 \xrightarrow{\text{Acetobacter}} \underset{\text{Acetic acid}}{CH_3COOH} + H_2O$$

Ethanoic acid is used in the manufacture of rayon and in plastic, rubber and silk industries. It also finds use as a solvent. Vinegar is used in cooking.

3. **Benzoic acid** is prepared by *oxidation* of toluene and other alkyl benzenes as discussed earlier. In the form of *esters*, benzoic acid is used in perfume industry. The salts of benzoic acid like *sodium benzoate* are used as *food preservatives*.

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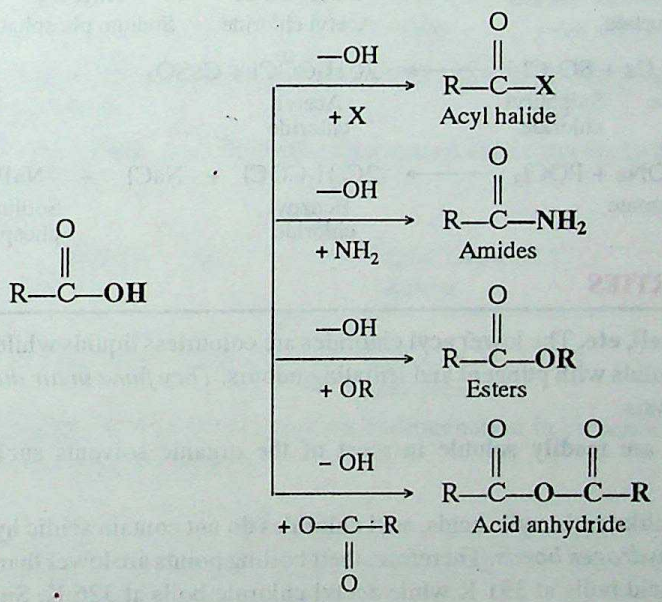
Distinction between Alcohols, Phenols and Carboxylic Acids

	Property	*Alcohols*	*Phenols*	*Carboxylic Acids*
1.	Action on litmus	No action	Turn blue litmus red	Turn blue litmus red
2.	Reaction with $NaHCO_3$	No reaction	No reaction	Brisk effervescence, evolution of CO_2
3.	Reaction with NaOH	No reaction	Form salts	Form salts
4.	Reaction with $FeCl_3$	No reaction	Give characteristic colours such as violet blue, red, etc.	No reaction

DERIVATIVES OF CARBOXYLIC ACID

Functional derivatives of acids refer to series of closely related organic compounds which can be structurally obtained by the replacement of *—OH* part of carboxyl group of the acids by *—X*, *—NH₂*, *—OR'* or *—OCOR* respectively.



8.19. ACYL CHLORIDES (R—C(=O)—Cl)

These are the derivatives of carboxylic acids in which *hydroxyl* (—OH) part of carboxyl group is replaced by *halo* group. The most reactive compounds among acyl halides are chloro compounds.

8.20. NOMENCLATURE

The names of acyl chlorides are derived from the **IUPAC** or **Common** names of the corresponding acids by replacing the suffix *ic acid* with *yl chloride*. Some examples are :

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Formula	*IUPAC Name*	*Common Name*
CH_3COCl	Ethanoyl chloride	Acetyl chloride
$CH_3CH_2CH_2COCl$	Butanoyl chloride	*n*-Butyryl chloride
C_6H_5COCl	Benzoyl chloride	Benzoyl chloride
$CH_3CH(Cl)COCl$	2-Chloropropanoyl chloride	α-Chloro propionyl chloride

8.21. METHODS OF PREPARATION

1. **From carboxylic acids.** As already discussed in section 8.17 acyl chloride can be prepared by the reaction of carboxylic acids with phosphorus pentachloride (PCl_5) or thionyl chloride ($SOCl_2$).

$$RCOOH + PCl_5 \longrightarrow RCOCl + POCl_3 + HCl$$

$$RCOOH + SOCl_2 \longrightarrow RCOCl + SO_2 + HCl$$

2. **From the salts of carboxylic acids.** Acyl chlorides can also be prepared by distillation of sodium or calcium salt of fatty acids with phosphorus trichloride, phosphoryl chloride or sulphuryl chloride.

$$\underset{\text{Sod. acetate}}{3CH_3COONa} + PCl_3 \longrightarrow \underset{\text{Acetyl chloride}}{3CH_3COCl} + \underset{\text{Sodium phosphate}}{Na_3PO_3}$$

$$\underset{\text{Cal. acetate}}{(CH_3COO)_2Ca} + \underset{\text{Sulphuryl chloride}}{SO_2Cl_2} \longrightarrow \underset{\text{Acetyl chloride}}{2CH_3COCl} + CaSO_4$$

$$\underset{\text{Sodium benzoate}}{2C_6H_5COONa} + POCl_3 \longrightarrow \underset{\text{Benzoyl chloride}}{2C_6H_5COCl} + NaCl + \underset{\text{Sodium meta-phosphate}}{NaPO_3}$$

8.22. PHYSICAL PROPERTIES

1. **Physical state, smell, etc.** The lower acyl chlorides are colourless liquids while the higher members are colourless low melting solids with pungent and irritating odours. *They fume in air due to the formation of hydrochloric acid by hydrolysis.*

2. **Solubility.** They are readily soluble in most of the organic solvents such as ether, benzene, chloroform, etc.

3. **Boiling points.** Unlike carboxylic acids, acyl chlorides do not contain acidic hydrogen. Hence, they do not form *intermolecular hydrogen bonds*. Therefore, their boiling points are lower than those of their parent acids. For example, acetic acid boils at 391 K while acetyl chloride boils at 326 K. Similarly, benzoic acid boils at 523 K while benzoyl chloride boils at 470 K.

8.23. CHEMICAL PROPERTIES

Acetyl chlorides are reactive class of compounds. Some of their chemical reactions are :

1. **Acylation reactions.** Acyl halides are vigorous acylating agents. They react :

with *water* to give *carboxylic* acids ; (*hydrolysis*)

with *alcohols* to give *esters* ; (*alcoholysis*)

with *ammonia* to give *amides* ; (*ammonolysis*)

with *carboxylic acids* or *carboxylate ions* to give *acid anhydrides*.

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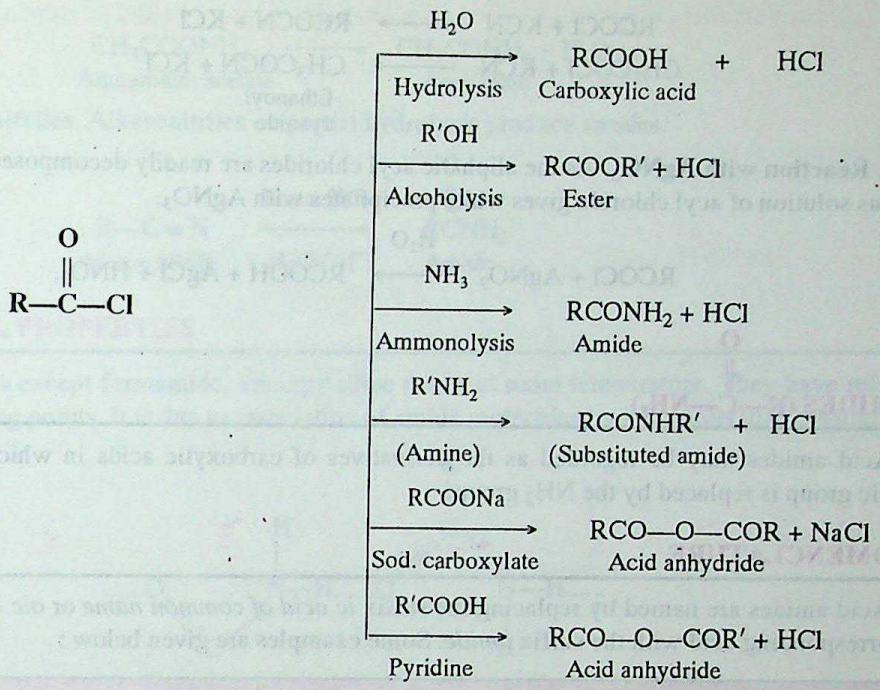

In the above reactions if the acid halide used is benzoyl chloride (C_6H_5COCl) then these reactions are termed as **benzoylation reactions.**

2. Friedal Craft's Acylation. Acyl chlorides on treatment with aromatic hydrocarbons in the presence of anhydrous $AlCl_3$ form ketones.

$$RCOCl + C_6H_6 \xrightarrow{AlCl_3} \underset{\text{Ketone}}{C_6H_5COR} + HCl$$

$$CH_3COCl + C_6H_6 \xrightarrow{AlCl_3} \underset{\text{Acetophenone}}{C_6H_5COCH_3} + HCl$$

3. Catalytic hydrogenation. Acyl chlorides on hydrogenation in presence of *Pd-BaSO₄* containing some *sulphur* or *quinoline* produce aldehydes.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-Cl + H_2 \xrightarrow{Pd/BaSO_4} RCHO + HCl$$

The reaction is known as **Rosenmund's reaction.**

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \xrightarrow{Pd/BaSO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + HCl$$

4. Reaction with dialkyl cadmium. Acyl halides react with dialkyl cadmium to form ketones.

$$2RCOCl + R_2'Cd \longrightarrow 2RCOR' + CdCl_2$$

$$2CH_3COCl + \underset{\text{Dimethyl cadmium}}{(CH_3)_2Cd} \longrightarrow \underset{\text{Acetone}}{2CH_3COCH_3} + CdCl_2$$

5. Reaction with KCN. Acyl chlorides react with potassium cyanide solution to form *alkanoyl cyanides.*

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$$RCOCl + KCN \longrightarrow RCOCN + KCl$$

$$CH_3COCl + KCN \longrightarrow \underset{\text{Ethanoyl cyanide}}{CH_3COCN} + KCl$$

6. Reaction with $AgNO_3$. As the aliphatic acyl chlorides are readily decomposed by water therefore an aqueous solution of acyl chloride gives white precipitates with $AgNO_3$.

$$RCOCl + AgNO_3 \xrightarrow{H_2O} RCOOH + AgCl + HNO_3.$$

8.24. AMIDES ($R—\overset{\overset{O}{\|}}{C}—NH_2$)

Acid amides may be regarded as the derivatives of carboxylic acids in which —OH part of the carboxylic group is replaced by the NH_2 group.

8.25. NOMENCLATURE

Acid amides are named by replacing the suffix *ic acid of common name* or *oic acid* of *IUPAC name* of the corresponding acid with the suffix *amide*. Some examples are given below :

Formula	*IUPAC Name*	*Common name*
$HCONH_2$	Methanamide	Formamide
CH_3CONH_2	Ethanamide	Acetamide
$CH_3CONH(CH_3)$	N-methylethanamide	N-methyl acetamide
$CH_3CH_2CONH_2$	Propanamide	Propionamide

8.26. PREPARATION OF AMIDES

1. From acid chlorides or acid anhydrides. Amides are generally prepared by reaction of *ammonia* or *amines* with *acid chlorides* or *acid anhydrides*.

$$RCOCl + NH_3 \longrightarrow \underset{\text{Amide}}{RCONH_2} + HCl$$

$$\underset{\text{Acid anhydride}}{(RCO)_2O} + 2NH_3 \longrightarrow RCOONH_4 + \underset{\text{Amide}}{RCONH_2}$$

$$\underset{\text{Acetic anhydride}}{(CH_3CO)_2O} + 2NH_3 \longrightarrow \underset{\text{Amm. acetate}}{CH_3COONH_4} + \underset{\text{Acetamide}}{CH_3CONH_2}$$

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + \underset{\text{Methyl amine}}{CH_3NH_2} \longrightarrow \underset{\text{N-Methyl acetamide}}{CH_3CONHCH_3} + HCl$$

2. From ammonium salts of carboxylic acids. Amides may also be prepared by the decomposition of ammonium salts of carboxylic acids.

$$\overset{\ominus}{R}COO\overset{\oplus}{N}H_4 \xrightarrow{\text{Heat}} RCONH_2 + H_2O$$

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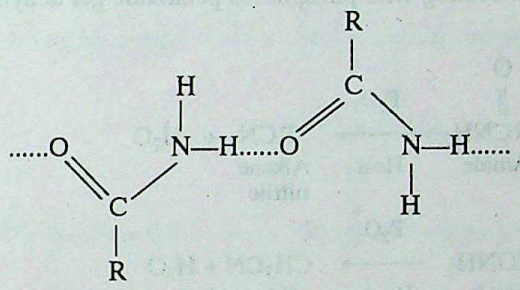
$$\underset{\text{Ammonium acetate}}{CH_3COONH_4} \xrightarrow{\text{Heat}} \underset{\text{Acetamide}}{CH_3CONH_2} + H_2O$$

3. From nitriles. Alkanenitriles on partial hydrolysis produce amides.

$$\underset{\text{Alkane nitrile}}{R{-}C{\equiv}N} \xrightarrow[H_2O/OH^-]{\text{Conc. HCl}} \underset{\text{Amide}}{R\overset{O}{\overset{\|}{C}}NH_2}$$

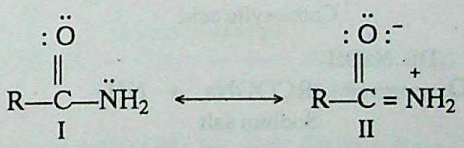
8.27. PHYSICAL PROPERTIES

All amides except formamide, are crystalline solids at room temperature. They have relatively high melting and boiling points. It is due to association of amide molecules by intermolecular hydrogen bonds.



8.28. CHEMICAL PROPERTIES

1. Amphoteric character. Amides are very *feeble bases*. This is due to the fact that the lone pair of electrons on nitrogen atom is involved in resonance with carbonyl group. It is due to the contribution of resonating structure II.



Thus, electron pair of nitrogen is not easily available for protonation. Consequently, the basic character is considerably decreased. However, under suitable conditions amides can also exhibit a feeble acidic character. The amphoteric character of amides is illustrated by the following reactions :

(*i*) *Basic character*. In accordance with resonating structure I already shown, it is evident that nitrogen atom of amide molecule has a lone pair of electrons. Therefore, it can act as a base. For example, acetamide (*as base*) reacts with hydrochloric acid (*an acid*) to form a salt.

$$\underset{\substack{\text{Acetamide}\\(Base)}}{CH_3CONH_2} + \underset{(Acid)}{HCl} \longrightarrow \underset{\substack{\text{Acetamide hydrochloride}\\(Salt)}}{CH_3CONH_2HCl}$$

(*ii*) *Acidic character*. In accordance with resonating structure II shown earlier, it is clear that the development of positive character on nitrogen atom facilitates the release of proton. Thus, amide can act as acid. For example, acetamide (*as acid*) reacts with mercuric oxide (*a base*) to form mercury salt and water.

$$\underset{\substack{\text{Acetamide}\\(Acid)}}{2CH_3CONH_2} + \underset{\substack{\text{Mercuric oxide}\\(Base)}}{HgO} \longrightarrow \underset{(Salt)}{(CH_3CONH)_2Hg} + \underset{(Water)}{H_2O}$$

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Similarly, acetamide reacts with metallic sodium to form sodium salt and hydrogen.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Na \longrightarrow \underset{\text{Sodium acetamide}}{CH_3CONH\overset{-}{}\overset{+}{Na}} + \frac{1}{2}H_2$$

2. Reduction. Amides on *reduction* with *sodium and ethyl alcohol* or with *lithium aluminium hydride*, form primary amines. For example :

$$\underset{\text{Amide}}{RCONH_2} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Primary amine}}{RCH_2NH_2} + H_2O$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2} + H_2O$$

3. Dehydration. Amides on heating with phosphorus pentoxide get dehydrated to form *nitriles*. For example :

$$\underset{\text{Amide}}{RC(=O)NH_2} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Alkane nitrile}}{RCN} + H_2O$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Ethanenitrile}}{CH_3CN} + H_2O$$

4. Hydrolysis. On boiling with dilute acid or alkali, amides rapidly undergo hydrolysis. For example :

$$\underset{\text{Amide}}{RCONH_2} + H_2O \xrightarrow{\text{Dil. HCl}} \underset{\text{Carboxylic acid}}{RCOOH} + NH_4Cl$$

$$\underset{\text{Amide}}{RCONH_2} + H_2O \xrightarrow{\text{Dil. NaOH}} \underset{\text{Sodium salt}}{RCOONa} + NH_3$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + H_2O \xrightarrow{\text{Dil. NaOH}} \underset{\text{Sodium benzoate}}{C_6H_5COONa} + NH_3$$

5. Reaction with nitrous acid. Amides react with nitrous acid to give carboxylic acids and nitrogen gas. Nitrous acid required is prepared in *situ* by reaction of $NaNO_2$ and HCl.

$$\underset{\text{Amide}}{R-C(=O)-NH_2} + \underset{\text{Nitrous acid}}{HONO} \xrightarrow{(NaNO_2/HCl)} \underset{\text{Carboxylic acid}}{R-C(=O)-OH} + N_2 + H_2O$$

6. Hoffmann's bromamide reaction. Amides (carrying primary nitrogen atom) react with bromine in the presence of alkali to form a *primary amine* carrying one carbon atom less than the parent amide.

$$\underset{\text{Amide}}{R-C(=O)-NH_2} + 4NaOH + Br_2 \longrightarrow \underset{\text{1-Amine}}{R-NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

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$$\underset{\text{Acetamide}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-NH_2} + 4NaOH + Br_2 \longrightarrow \underset{\text{Methylamine}}{CH_3NH_2} + 2NaBr + Na_2CO_3 + 2H_2O$$

This reaction is useful in the preparation of a lower homologue from the higher one (descending of series).

Mechanism of Bromamide Reaction

The bromamide reaction is believed to proceed by following steps :

$$NaOH + Br_2 \longrightarrow \overset{+}{Na}\overset{-}{O}Br + \overset{+}{Na}\overset{-}{Br} + H_2O$$

(*i*) $$R-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{N}H_2 + \overset{-}{O}Br \longrightarrow \underset{\text{N-Bromoamide}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\ddot{N}}-Br + \overset{-}{O}H}$$

(*ii*) $$R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle H}{|}}{\ddot{N}}-Br + \overset{-}{O}H \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle \cdot\cdot}{}}{\ddot{N}^{-}}-Br + H_2O$$

(*iii*) $$R-\overset{\overset{\displaystyle O}{\|}}{C}-\underset{\underset{\displaystyle \cdot\cdot}{}}{\ddot{N}^{-}}-Br \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{N}: + \overset{-}{Br}:$$

(*iv*) $$R-\overset{\overset{\displaystyle O}{\|}}{C}-\ddot{N} \xrightarrow{\text{Rearrangement}} \underset{\text{Alkylisocyanate}}{R-N=C=O}$$

(*v*) $$R-N=C=O + 2NaOH \longrightarrow RNH_2 + Na_2CO_3$$

8.29. ESTERS ($R\overset{\overset{\displaystyle O}{\|}}{C}OR'$)

Esters are the derivatives of the carboxylic acids in which the —OH part of the carboxylic group has been replaced by —OR group where, R may be *alkyl* or *aryl* group.

8.30. NOMENCLATURE

The esters are named by writing the name of the *alkyl* or *aryl* group of —OR′ part of the molecule before the name of the parent acid and replacing the suffix *ic* of the (*IUPAC* or *common*) name of the acid by *ate*, some examples are :

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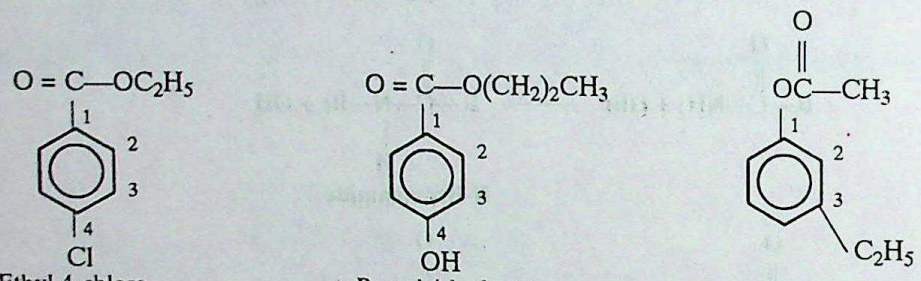
Formula	*IUPAC name*	*Common name*
$HCOOC_2H_5$	Ethyl methanoate	Ethyl formate
$CH_3COOC_2H_5$	Ethyl ethanoate	Ethyl acetate
$CH_3COOC_6H_5$	Phenyl ethanoate	Phenyl acetate
$\overset{\gamma}{\underset{4}{CH_3}}\overset{\beta}{\underset{3}{CH_2}}—\overset{\alpha}{\underset{2}{CH}}(Br)—\overset{}{\underset{1}{COOCH_3}}$	Methyl-2-bromo-butanoate	Methyl, α-bromo-butyrate

The names of some aromatic esters are given below :



Ethyl 4-chloro benzoate — *n*-Propyl 4-hydroxy benzoate — (3-Ethyl phenyl) ethanoate

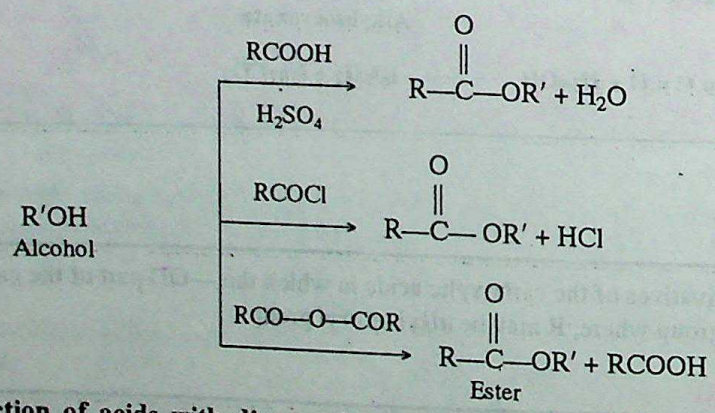
8.31. PREPARATION OF ESTERS

1. Acylation. Esters are prepared by the *acylation of alcohols* or *phenols*. The acylating agents can be any of the following.

Carboxylic acid/H_2SO_4 or

Acyl chloride or

Acid anhydride



2. By reaction of acids with diazomethane. Acids on being treated with ethereal solution of diazomethane yield methyl esters.

$$\underset{\text{Acid}}{RCOOH} + \underset{\text{Diazo methane}}{CH_2N_2} \longrightarrow \underset{\text{Ester}}{RCOOCH_3} + N_2$$

3. By Tischenko reaction. When aldehydes containing α-hydrogen atoms are treated with aluminium ethoxide. They undergo condensation to produce esters.

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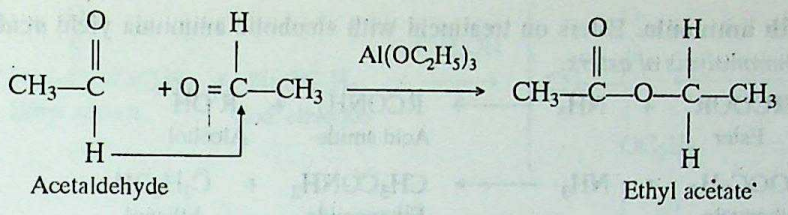


8.32. PHYSICAL PROPERTIES OF ESTERS

1. Esters are colourless, oily liquids with a characteristic fruity odour. The odour of the most of the flowers and fruits is due to esters present in them. The characteristic tastes and odours of different esters find applications in the manufacture of artificial flavouring and perfuming agents. The flavours of some of the esters are given below :

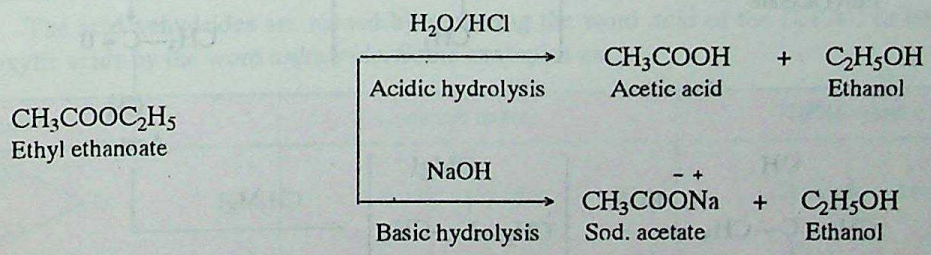
Ester	*Flavour*	*Ester*	*Flavour*
n-Pentyl ethanoate	Banana	Amyl butyrate	Apricot
Octyl ethanoate	Orange	Isobutyl methanoate	Raspberry
Ethyl butanoate	Pineapple	Benzyl ethanoate	Jasmine

2. Esters are sparingly soluble in water but are quite miscible in organic solvents like alcohols and ethers. In fact, most of the esters are themselves very good solvents for plastics and nitrocellulose.

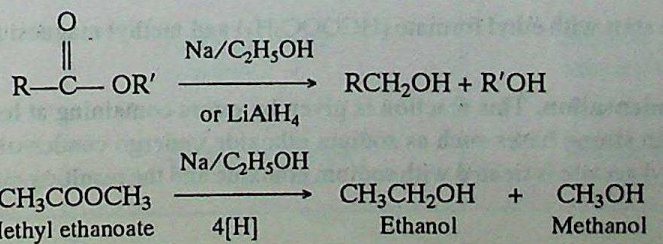
3. The boiling points of esters are always less than the corresponding carboxylic acids because esters do not form hydrogen bonds.

8.33. CHEMICAL PROPERTIES

1. **Hydrolysis.** Esters are hydrolysed slowly by water at boiling temperature. The reaction is catalysed by small amount of *acid* or *base*. The basic hydrolysis is also known as **saponification.** It is because of the fact that the esters with high molecular mass acids (C_{12}—C_{17}) give soap on hydrolysis with a base. **Soaps** are sodium or potassium salts of carboxylic acids with high molecular mass (C_{12}—C_{17}).



2. **Reduction.** Esters are reduced to alcohols by the reducing agents like (*sodium/ethanol*) or (*lithium aluminium hydride*).



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3. Reaction with ammonia. Esters on treatment with alcoholic ammonia yield *acid amides*. This reaction is known as *ammonolysis of esters*.

$$\underset{\text{Ester}}{RCOOR'} + NH_3 \longrightarrow \underset{\text{Acid amide}}{RCONH_2} + \underset{\text{Alcohol}}{R'OH}$$

$$\underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + NH_3 \longrightarrow \underset{\text{Ethanamide}}{CH_3CONH_2} + \underset{\text{Ethanol}}{C_2H_2OH}$$

4. Reaction with phosphorus pentachloride. Esters are converted into acid chlorides and alkyl halides by heating with phosphorus pentachloride.

$$RCOOR' + PCl_5 \longrightarrow RCOCl + R'Cl + POCl_3$$

$$\underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + PCl_5 \longrightarrow \underset{\text{Benzoyl chloride}}{C_6H_5COCl} + C_2H_5Cl + POCl_3$$

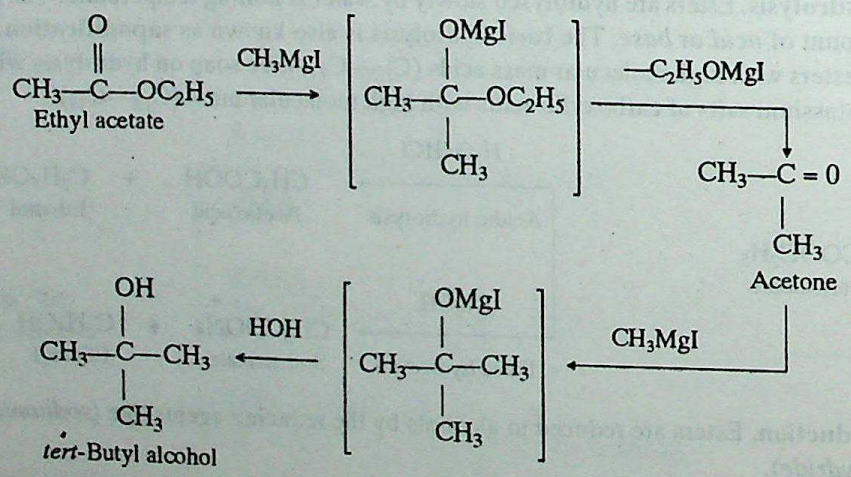
5. Alcoholysis. An ester on refluxing with a large excess of an alcohol in the presence of a little acid or alkali, undergoes exchange of alcohol residues, *i.e.*, *alkoxy parts* as shown below :

$$\underset{\text{Ester}}{RCOOR'} + \underset{\text{Alcohol}}{R''OH} \overset{H^+}{\rightleftharpoons} RCOOR'' + R'OH$$

$$\underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + \underset{\text{Methanol}}{CH_3OH} \overset{H^+}{\rightleftharpoons} \underset{\text{Methyl ethanoate}}{CH_3COOCH_3} + \underset{\text{Ethanol}}{C_2H_5OH}$$

This reaction is known as *alcoholysis* or *trans-esterification.*

6. Reaction with Grignard's reagent. All esters except the esters of formic acid react with Grignard's reagent to give tertiary alcohols. However, the esters of formic acid, *i.e.*, *alkyl formates* form secondary alcohols.



Similarly, if we start with ethyl formate ($HCOOC_2H_5$) and methyl magnesium iodide, the product will be *isopropyl alcohol.*

7. Claisen Condensation. This reaction is given by esters containing at least one α-hydrogen. Such esters when treated with strong bases such as sodium ethoxide undergo condensation to form β-keto esters. For example, when ethyl acetate is treated with sodium ethoxide and the resulting mixture is acidified, it yields ethyl acetoacetate.

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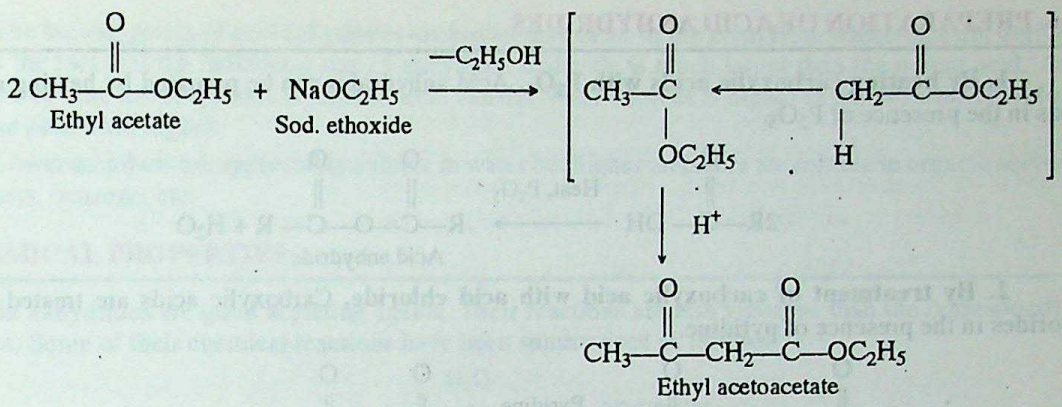
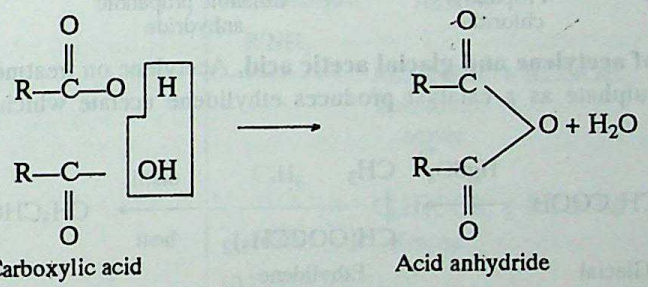


8.34. ACID ANHYDRIDES (R—C(=O)—O—C(=O)—R)

Acid anhydrides are considered to be derived from carboxylic acids by the removal of a molecule of water from the two molecules of the acid.



8.35. NOMENCLATURE

The acid anhydrides are named by replacing the word *acid* of the IUPAC or common name of the carboxylic acids by the word *anhydride*. Some examples are :

Formula	*Common names*	*IUPAC names*
$(CH_3CO)_2O$	Acetic anhydride	Ethanoic anhydride
$(C_2H_5CO)_2O$	Propionic anhydride	Propanoic anhydride
$(CH_3CO)(C_2H_5CO)O$	Acetic propionic anhydride	Ethanoic propanoic anhydride
$(C_6H_5CO)_2O$	Benzoic anhydride	Benzoic anhydride

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8.36. PREPARATION OF ACID ANHYDRIDES

1. By heating carboxylic acids with P_2O_5. Acid anhydrides can be prepared by heating carboxylic acids in the presence of P_2O_5.

$$2R-\overset{\overset{\displaystyle O}{\|}}{C}-OH \xrightarrow{\text{Heat, } P_2O_5} \underset{\text{Acid anhydride}}{R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R} + H_2O$$

2. By treatment of carboxylic acid with acid chloride. Carboxylic acids are treated with acid chlorides in the presence of pyridine.

$$R-\overset{\overset{\displaystyle O}{\|}}{C}-OH + R'-\overset{\overset{\displaystyle O}{\|}}{C}-Cl \xrightarrow{\text{Pyridine}} R-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-R' + HCl$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Acetyl chloride}}{CH_3COCl} \xrightarrow{\text{Pyridine}} \underset{\text{Acetic anhydride}}{CH_3CO-O-COCH_3} + HCl$$

$$\underset{\text{Acetic acid}}{CH_3COOH} + \underset{\text{Propanoyl chloride}}{C_2H_5COCl} \xrightarrow{\text{Pyridine}} \underset{\text{Ethanoic propanoic anhydride}}{CH_3CO-O-COC_2H_5} + HCl$$

3. By reaction of acetylene and glacial acetic acid. Acetylene on treatment with acetic acid in the presence of mercuric sulphate as a catalyst produces ethylidene acetate which on distillation produces anhydride.

$$\underset{\text{Acetylene}}{CH\equiv CH} + \underset{\text{Glacial acetic acid}}{2CH_3COOH} \xrightarrow{HgSO_4} \underset{\text{Ethylidene acetate}}{CH_3-CH(OOCCH_3)_2} \xrightarrow[\text{heat}]{\text{distil}} CH_3CHO + \underset{\text{Acetic anhydride}}{(CH_3CO)_2O}$$

4. By pasing ketone into glacial acetic acid

$$\underset{\text{Ketene}}{CH_2=C=O} + \underset{\text{Acetic acid}}{CH_3COOH} \longrightarrow \underset{\text{Acetic anhydride}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-O-\overset{\overset{\displaystyle O}{\|}}{C}-CH_3}$$

Ketene required for the reaction can be obtained by high temperature dehydration of acetic acid or by pyrolysis of acetone at 950-1030 K.

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[\text{1075 K}]{AlPO_4} \underset{\text{Ketene}}{CH_2=C=O} + H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} \xrightarrow{\text{950—1030 K}} \underset{\text{Ketene}}{CH_2=C=O} + CH_4$$

8.37. PHYSICAL PROPERTIES

1. Lower aliphatic anhydrides are colourless liquids with sharp irritating small. Aromatic anhydrides, on the other hand, are colourless solids.

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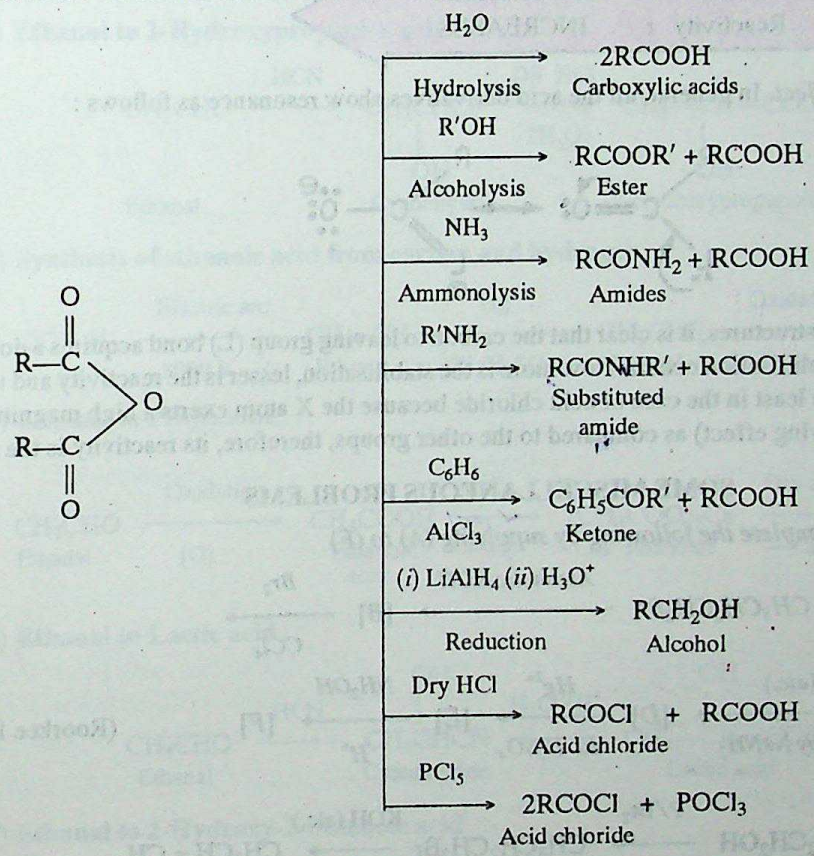
2. The boiling points of acid anhydrides are higher than those of the acids from which they are derived. It is due to the fact that the molecular size of anhydride molecule is much larger than the parent acid. As a consequence of this, the magnitude of interparticle van der Waal's forces is higher in anhydrides. Therefore, their boiling points are higher.

3. Lower members are appreciably soluble in water but higher members are soluble in organic solvents such as ethers, benzene, etc.

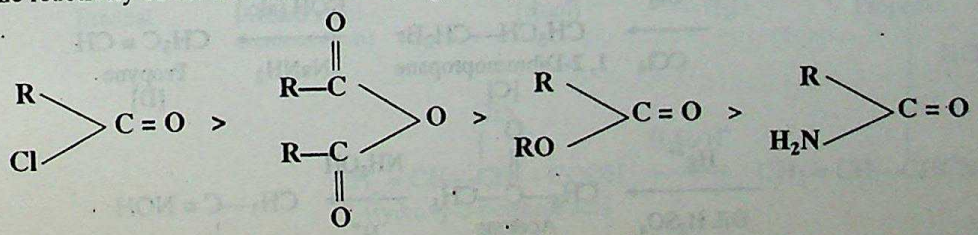
8.38. CHEMICAL PROPERTIES

Acid anhydrides are good acylating agents. Their reactions are less vigorous than the corresponding acyl halides. Some of their chemical reactions have been summarised as follows :



Relative Reactivity of Acid Derivatives

The reactivity of the acid derivatives, in general, follows the order :



REACTIVITY DECREASES

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The above order of reactivity can be explained in terms of the

(*i*) *basicity of leaving groups* and (*ii*) *resonance effects.*

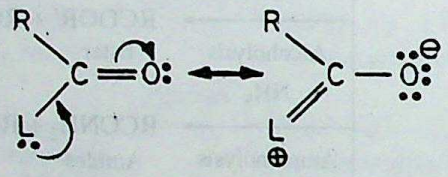
(*i*) *Basicity of leaving groups.* Weaker the basic character of the leaving group (anion) is, more will be the ease with which the bond can be ruptured and hence more is the reactivity. Among the given compounds Cl^- ion is the weakest base and hence chlorides are most reactive.

The correct order of basicity of the leaving group and their tendency to leave is

$$H_2\bar{N}: \quad > \quad :\bar{O}R \quad > \quad RCO\bar{O}: \quad > \quad :\bar{Cl}$$

Basicity : DECREASES
Reactivity : INCREASES

(*ii*) *Resonance effect.* In general, all the acid derivatives show resonance as follows :



In the resonating structures, it is clear that the carbon to leaving group (L) bond acquires a double bond character due to which stabilisation occurs. Now more is the stabilisation, lesser is the reactivity and *vice versa.* As the stabilisation is the least in the case of acid chloride because the X atom exerts a high magnitude of —I effect (electron withdrawing effect) as compared to the other groups, therefore, its reactivity is the most.

SOME MISCELLANEOUS PROBLEMS

Example 8.1. *Complete the following by supplying (A) to (F)*

$$[A] \xrightarrow{P/Br_2} CH_3CH_2CH_2Br \xrightarrow{\text{Alcoholic KOH}} [B] \xrightarrow[CCl_4]{Br_2}$$

$$[C] \xrightarrow[\text{Followed by } NaNH_2]{KOH\ (alc.)} [D] \xrightarrow[\text{dil. } H_2SO_4]{Hg^{2+}} [E] \xrightarrow[H^+]{NH_2OH} [F]$$

(Roorkee Ent. 1990)

Solution.

$$\underset{\substack{\text{1-Propanol}\\ [A]}}{CH_3CH_2CH_2OH} \xrightarrow{P/Br_2} \underset{\text{1-Bromopropane}}{CH_3CH_2CH_2Br} \xrightarrow{KOH\ (alc.)} \underset{\substack{\text{Propene}\\ [B]}}{CH_3CH = CH_2}$$

$$\xrightarrow[CCl_4]{Br_2} \underset{\substack{\text{1, 2-Dibromopropane}\\ [C]}}{CH_3\overset{Br}{\overset{|}{C}}H—CH_2Br} \xrightarrow[NaNH_2]{KOH\ (alc.)} \underset{\substack{\text{Propyne}\\ [D]}}{CH_3C \equiv CH}$$

$$\xrightarrow[\text{Dil. } H_2SO_4]{Hg^{2+}} \underset{\substack{\text{Acetone}\\ [E]}}{CH_3—\overset{O}{\overset{\|}{C}}—CH_3} \xrightarrow[H^+]{NH_2OH} \underset{\substack{\text{Acetoxime}\\ [F]}}{CH_3—\underset{\underset{CH_3}{|}}{C} = NOH}$$

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Example 8.2. *Bring out the following conversions :*

(*i*) *Ethanol to 2-Hydroxypropanoic acid* (*ii*) *Carbon and Hydrogen to Ethanoic acid*

(*iii*) *Ethanol to Propanone* (*iv*) *Ethanal to Lactic acid* (Roorkee Ent. 1986)

(*v*) *Ethanal to 2-hydroxy-3-butenoic acid* (I.I.T. 1990)

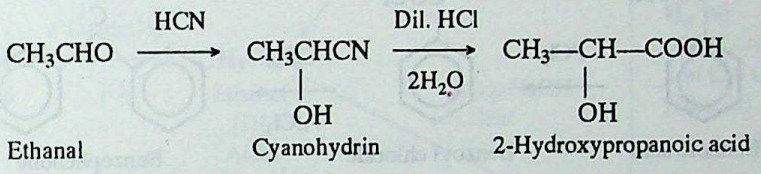
(*vi*) *Benzamide to Toluene* (*vii*) *Benzoic acid to Benzophenone*

(*viii*) *Acetone to 2-Methyl-2-propanol* (A.I. CBSE 1990)

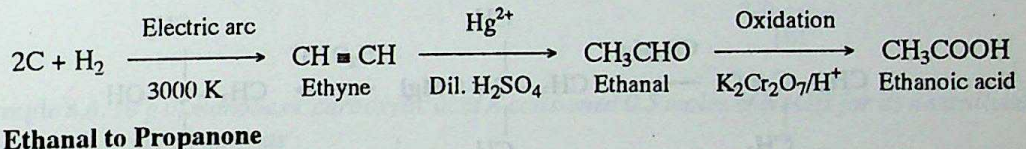
(*ix*) *Malonic acid to Acetic acid.* [A.I. CBSE (4) 1992]

Solution.

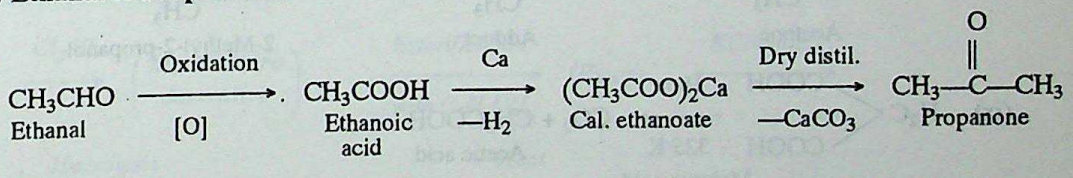
(*i*) **Ethanol to 2-Hydroxypropanoic acid**



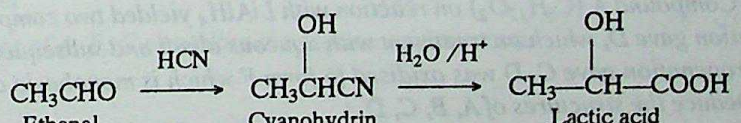
(*ii*) **Synthesis of ethanoic acid from carbon and hydrogen**



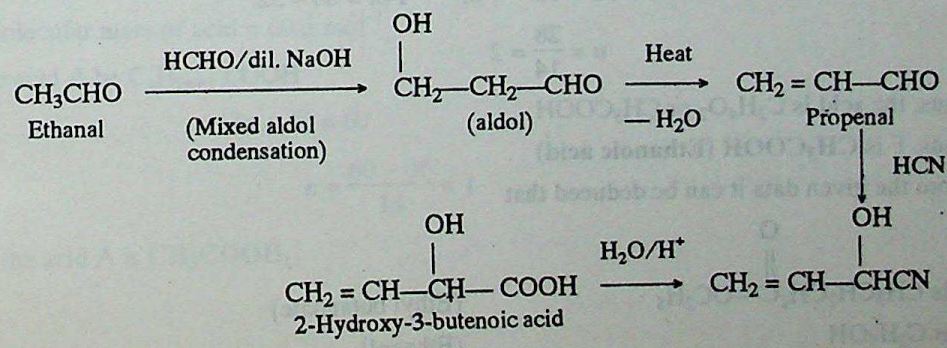
(*iii*) **Ethanal to Propanone**



(*iv*) **Ethanal to Lactic acid**



(*v*) **Ethanal to 2-Hydroxy-3-butenoic acid**



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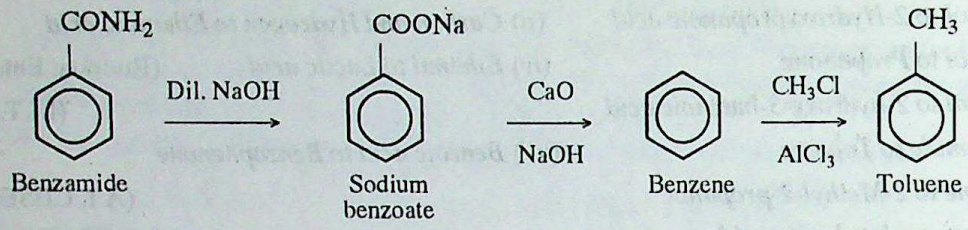
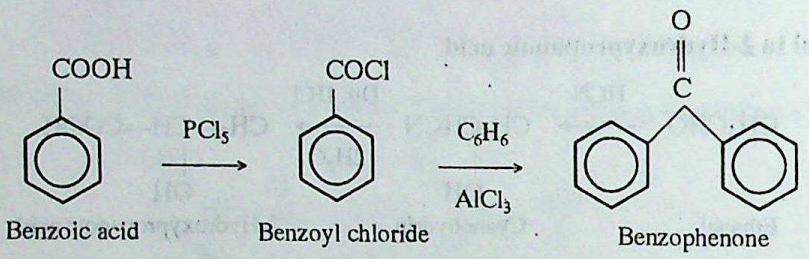
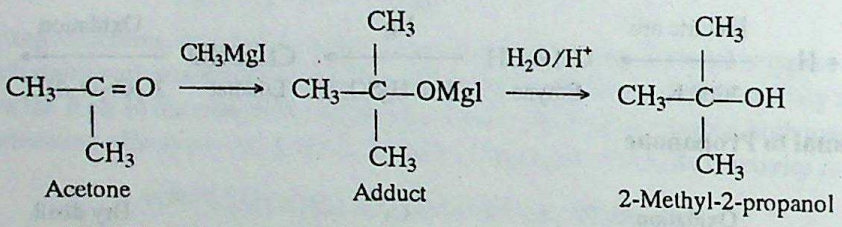
(*vi*) Benzamide to Toluene



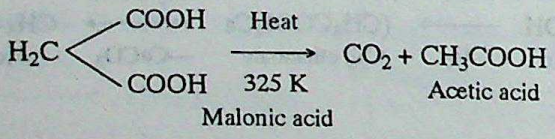
(*vii*) Benzoic acid to Benzophenone



(*viii*) Acetone to 2-Methyl-2-propanol



(*ix*)



Example 8.3. *Compound A ($C_6H_{12}O_2$) on reaction with $LiAlH_4$ yielded two compounds B and C. The compound B on oxidation gave D, which on treatment with aqueous alkali and subsequent heating furnished E. E on catalytic hydrogenation gave C. D was oxidised to form F which is monobasic carboxylic acid with molecular mass 60. Deduce the structures of A, B, C, D.* (I.I.T.J.E.E. 1990)

Solution. Let the monobasic carboxylic acid, F be $C_nH_{2n}O_2$.

$\therefore$ $14n + 32 = 60$ or $14n = 60 - 32$

$$n = \frac{28}{14} = 2$$

Thus, the acid is $C_2H_4O_2$ or CH_3COOH

Thus, F is **CH_3COOH (Ethanoic acid)**

From the given data it can be deduced that

A is $CH_3CH_2CH_2\overset{\overset{\displaystyle O}{\|}}{C}—OC_2H_5$ (Ethyl butanoate)

B is C_2H_5OH (Ethanol)

C is $CH_3CH_2CH_2CH_2OH$ (1-Butanol)

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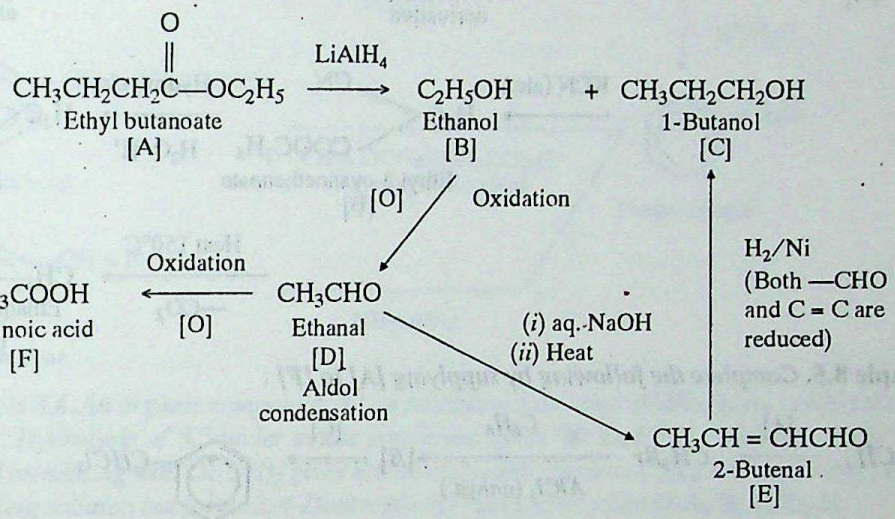
D is CH_3CHO (Ethanal)

E is $CH_3CH = CHCHO$ (2-Butenal)

F is CH_3COOH (Ethanoic acid)

The sequence of reactions is as under :



Example 8.4. *30 g of monobasic carboxylic acid A consumed 0.5 moles of NaOH for its neutralisation. A is subjected to following treatments :*

$$[A] \xrightarrow{Cl_2/P} \left(\begin{matrix}\textit{Monochloro}\\ \textit{derivative}\end{matrix}\right) \xrightarrow[\textit{with } C_2H_5OH]{\textit{Esterification}} (\textit{Ester}) \xrightarrow{KCN\ (alc.)}$$

$$[B] \xrightarrow[\textit{Acid}]{\textit{Hydrolysis}} \textit{Dicarboxylic acid } [C] \xrightarrow[150°C]{\textit{Heat}} A$$

Give structures of A, B, C providing the sequence of reactions.

Solution.

0.5 mol of NaOH is required for acid = 30 g

1 mol of NaOH is required for acid = 60 g

$\therefore$ Molecular mass of acid = 60 g mol^{-1}

Let the acid A be $C_nH_{2n+1}COOH$

$$\therefore \quad 14n + 46 = 60$$

or

$$n = \frac{60 - 46}{14} = 1$$

Thus, the acid A is **CH_3COOH.**

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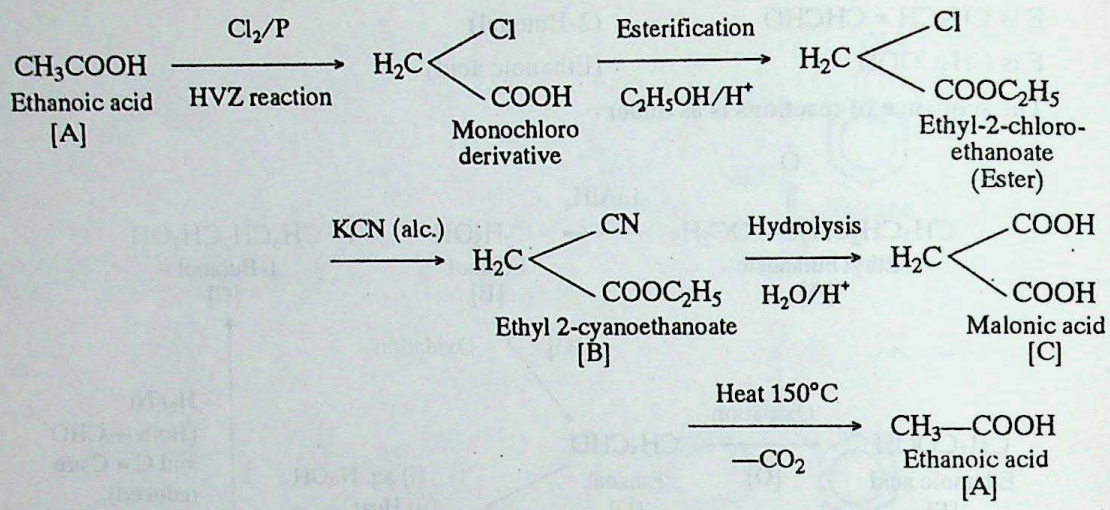
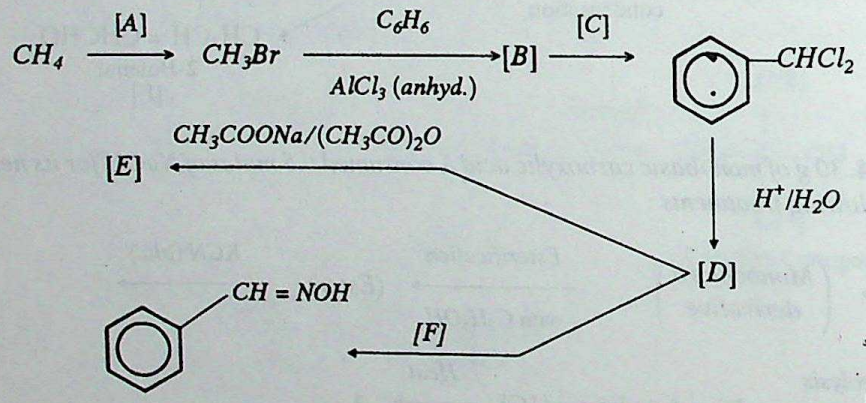
The sequence of reactions is as follows :



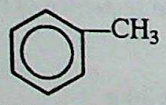
Example 8.5. *Complete the following by supplying [A] to [F] :*



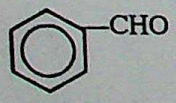
(Roorkee Ent. 1991)

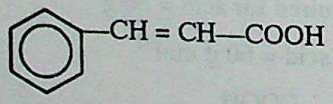
Solution. In the above sequence,

[A] is Br_2

[B] is  Toluene

[C] is Cl_2 (g)

[D] is  Benzaldehyde ;

[E] is  Cinnamic acid

[F] is NH_2OH/H^+

The sequence of reactions is :

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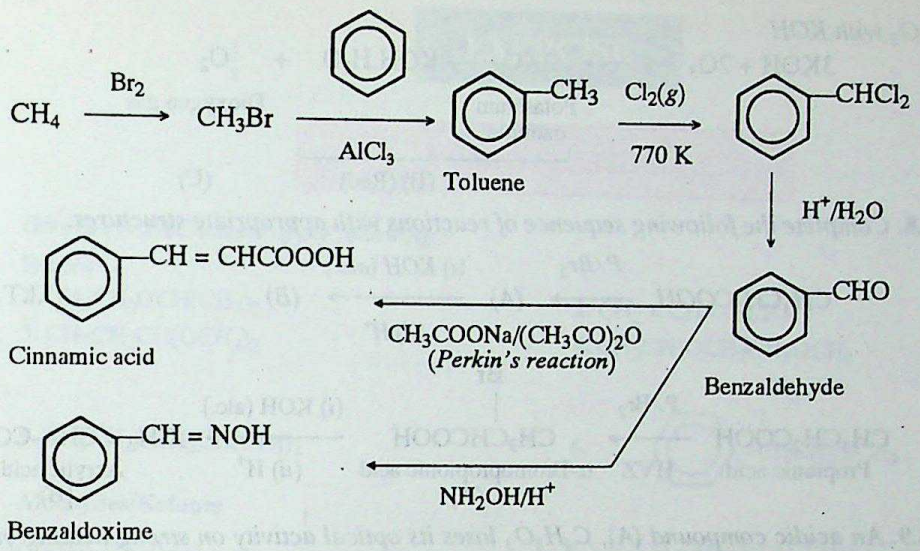
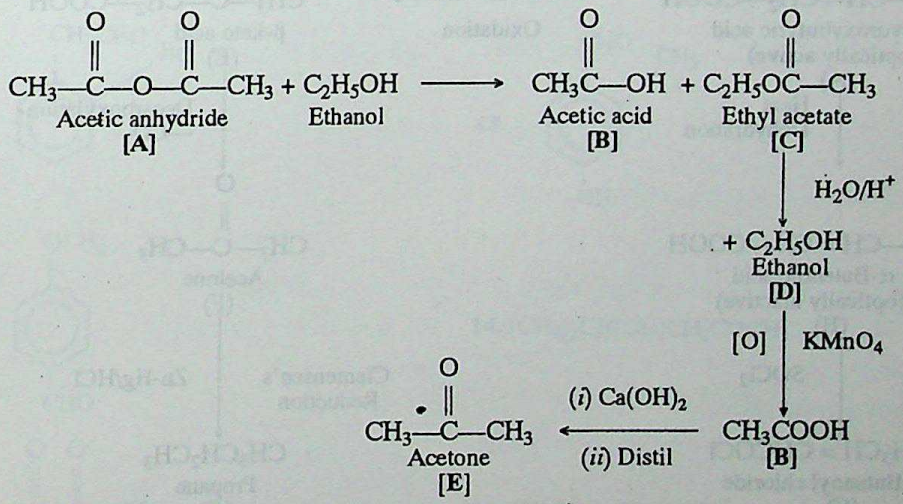


Example 8.6. *An organic compound* **'A'** *on treatment with ethyl alcohol gives carboxylic acid* **'B'** *and compound* **'C'**. *Hydrolysis of* **'C'** *under acidic conditions gives* **'B'** *and* **'D'**. *Oxidation of* **'D'** *with* $KMnO_4$ *also gives* **B. B** *on heating with* $Ca(OH)_2$ *gives* **E** *with molecular formula* C_3H_6O. **E** *does not give Tollen's test or reduce Fehling solution but forms 2, 4-Dinitrophenyl hydrozone. Identify* **A, B, C, D, E.**

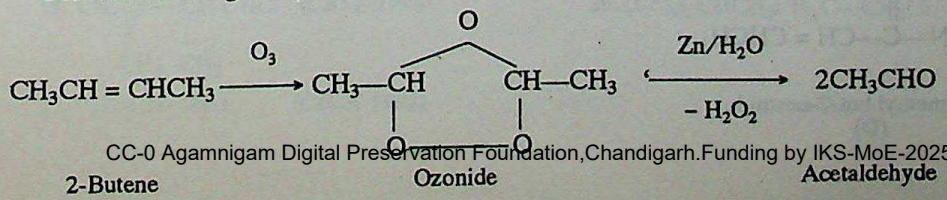
(I.I.T.J.E.E. 1992)

Solution. Since **E** does not give Tollen's test or Fehling test. Therefore, it is a ketone. The sequence of reactions is :



Example 8.7. *When a gas* **A** *is passed through dry KOH at low temperature, a deep red coloured compound* **B** *and a gas* **C** *are obtained. The gas* **A** *on reaction with but-2-ene followed by treatment with* Zn/H_2O *yields acetaldehyde. Identify A, B, C.* (I.I.T. 1994)

Solution. Since gas A produces acetaldehyde from 2-Butene, it must be ozone. The reaction are



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Reaction of O_3 with KOH

$$3KOH + 2O_3 \longrightarrow \underbrace{2KO_3 + KOH.H_2O}_{\text{(B) (Red)}} + \underset{\text{(C)}}{\tfrac{1}{2}O_2}$$

Potassium ozonide — Dioxygen gas

Example 8.8. *Complete the following sequence of reactions with appropriate structures.*

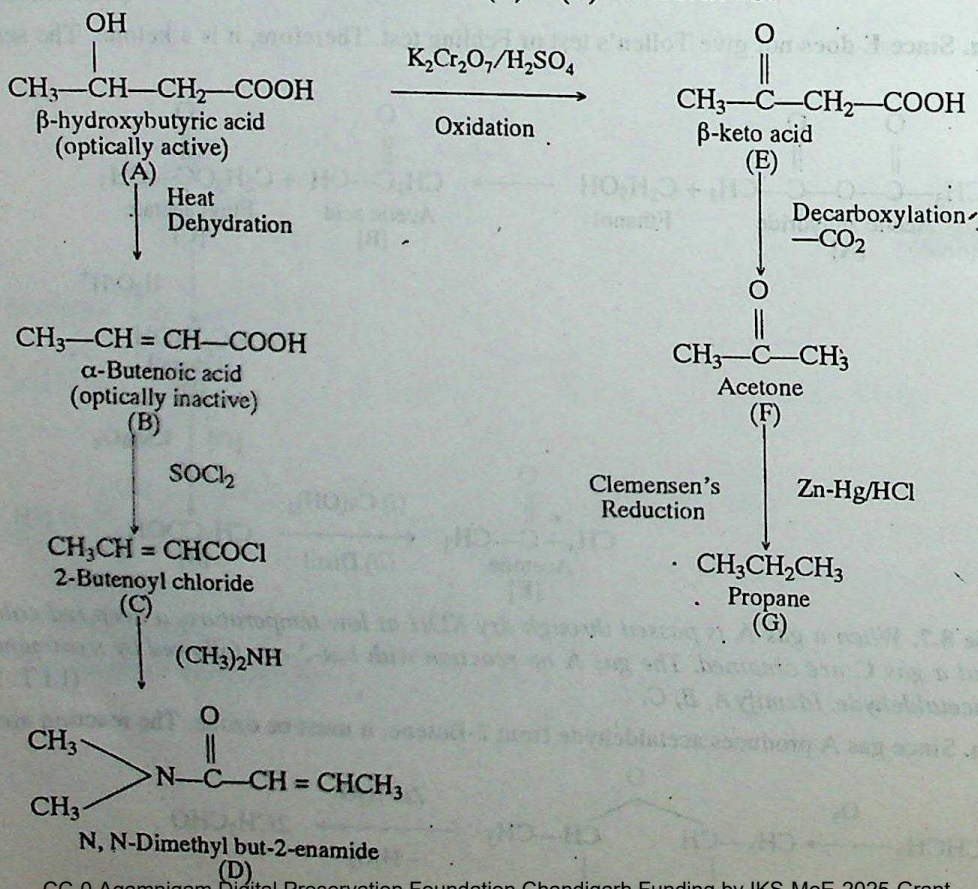
$$CH_3CH_2COOH \xrightarrow{P/Br_2} (A) \xrightarrow[(ii)\ H^+]{(i)\ KOH\ (alc.)} (B)$$ (I.I.T. 1995)

Solution.

$$\underset{\text{Propionic acid}}{CH_3CH_2COOH} \xrightarrow[\text{HVZ}]{P/Br_2} \underset{\text{α-Bromopropionic acid (A)}}{CH_3\overset{\overset{Br}{|}}{C}HCOOH} \xrightarrow[(ii)\ H^+]{(i)\ KOH\ (alc.)} \underset{\text{Acrylic acid (B)}}{CH_2 = CH—COOH}$$

Example 8.9. *An acidic compound (A), $C_4H_8O_3$ loses its optical activity on strong heating yielding (B), $C_4H_6O_2$ which reacts readily with $KMnO_4$ and decolourises it. (B) forms a derivative (C) with $SOCl_2$ which on reaction with $(CH_3)_2NH$ gives (D). The compound (A) also forms unstable compound (E) on treatment with dilute chromic acid (E) decarboxylate readily to give (F) C_3H_6O which on treatment with amalganated zinc and HCl gives hydrocarbon (G). Give structures of (A) to (G).* (Roorkee 1995)

Solution. The sequence of reactions from (A) to (G) are as follows :



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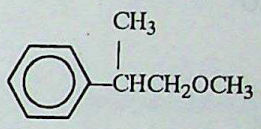
EXERCISE

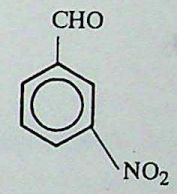
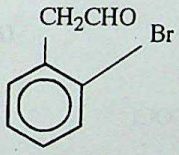
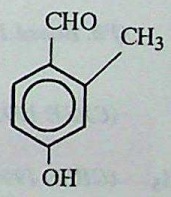
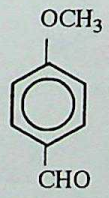
NOMENCLATURE

Give the IUPAC names of the following :

Ethers

1. $CH_3CH_2OCH(CH_3)_2$
2. $CH_2 = CH—OCH_3$
3. $CH_3CH_2CH(OCH_3)_2$
4. $CH_3CH_2OCH_2CH_2OCH_3$
5. $CH_3CH_2OCH_2CH(CH_3)_2$
6. 

Aldehydes/Ketones

7. $CH_3CH(C_2H_5)COCH_3$
8. $CH_3CH_2CH_2CH(C_2H_5)CH_2CHO$
9. $CH_3COCH(C_2H_5)CH_2CH_2Cl$
10. 
11. 
12. 
13. 
14. $(CH_3)_2CH(OH)CH_2COCH_3$
15. $CH_3—C(=O)—C(=O)—CH_3$
16. $CH_3CH = CH—CHO$
17. $(CH_3)_2CHCH_2CHO$ *(Pb. Board 1993)*
18. $(CH_3)_2CHCOCH(CH_3)_2$ *(CBSE 1994)*
19. $CH_3CH(CH_3)—CH(CH_3)CHO$ *(CBSE 1994)*
20. $(CH_3)_2CHCH_2CH_2C(=O)—CH_2Cl$ *(Roorkee 1992)*
21. $C_6H_5CH_2CHO$ *(CBSE 1992)*

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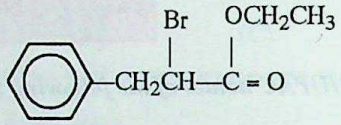
Carboxylic acids and their derivatives

22. $\begin{array}{c} COOH \\ | \\ COOH \end{array}$

23. $(CH_3)_2CHCH_2CO_2H$

24. $CH_3-\underset{}{\overset{Cl}{\overset{|}{C}}}H-\overset{Cl}{\overset{|}{C}}=O$

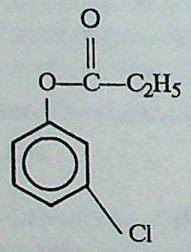
25. 

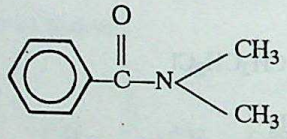
26. $(C_6H_5CO)_2O$

27. $CH_3CH_2\underset{CH_3}{\underset{|}{N}}-\overset{O}{\overset{\|}{C}}-H$

28. $(CH_3)_2CH\overset{O}{\overset{\|}{C}}-NH_2$

29. $\begin{array}{l} CH(OH)COOH \\ | \\ CH(OH)COOH \end{array}$

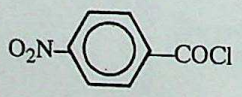
30. 

31. 

32. CH_3COCH_2COOH (*Pb. Board 1993*)

33. CHO.COOH (*Pb. Board 1993*)

34. $CH_3CH(OH)COOH$ (*CBSE 1992*)

35.  (*CBSE 1991*)

36. $CH_3CH_2\underset{CH_3}{\underset{|}{C}}H\ COOC_2H_5$ (*CBSE 1994*)

37. ***Write the structures and IUPAC names of the following compounds :***

(*i*) Di-isopropyl ether
(*ii*) N, N-Diethyl formamide
(*iii*) Lactic acid
(*iv*) Pyruvic acid
(*v*) Isopropyl methyl ketone
(*vi*) Acrolein.

38. ***Write structural formulae for the following :***

(*i*) Pinacol
(*ii*) Pinacolone
(*iii*) *n*-Valeric acid
(*iv*) Acetamide
(*v*) Malonic acid
(*vi*) Succinic acid.

VERY SHORT ANSWER QUESTIONS

1. An organic acid X is heated with soda lime to produce ethane as the product. The acid X is ?

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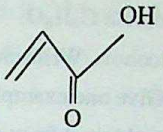
2. What is the correct IUPAC name of  ?

3. How will you change acetic acid to glycine ?
4. What is Rosenmund's reduction ?
5. What is alternation effect ? How it governs the m.p. of acids.
6. How can the presence of carboxylic acid be detected. Give equation.
7. What is H.V.Z. reaction ?
8. What is vinegar ?
9. What do you understand by trans esterification reaction ?
10. Name the two functional isomers that could be obtained from the compound with formula $C_3H_6O_2$.
11. Why acetyl chloride is a highly reactive compound ?
12. What is Tischenko reaction ?
13. What is glacial acetic acid ?
14. How will you convert ethyne to acetic anhydride ?
15. Why formic acid is more stronger than acetic acid ?
16. Why acids evolved CO_2 on reaction with carbonates ?
17. Name a reagent used to oxidise propionic acid to
    (*i*) pyruvic acid (*ii*) β-hydroxy propionic acid.
18. Benzoic acid is stronger than acetic acid, why ?
19. What is quick vinegar process, explain ?
20. Convert benzoyl chloride to benzoic acid.

DESCRIPTIVE QUESTIONS

Ethers

1. Give the general formula of *ethers*.
2. Write the structure of :
   (*i*) Anisole (*ii*) Phenetole
   (*iii*) Methyl tertiary butyl ether (*iv*) A five-membered cyclic ether.
3. Write a note on Williamson's synthesis for ethers. Can we use tertiary butyl chloride and sodium ethoxide to prepare ethyl tert, butyl ether. Justify your answer.
4. Give the mechanism of cleavage of ethyl methyl ether with HI.
5. How does diethyl ether react with :
   (*i*) PCl_5 (*ii*) H_2SO_4 (*iii*) HI.
6. Give reasons for the following :
   (*i*) The boiling points of ethers are lower than their isomeric alcohols.
   (*ii*) The order of reactivity of halogen acids with ethers is HI > HBr > HCl.
   (*iii*) Phenyl methyl ether reacts with HI to give phenol and methyl iodide and not phenyl iodide and methyl alcohol.

[*CBSE (2) 1992*]

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7. Give two functional isomers of compound with formula C_3H_6O.
8. Give two methods of preparation of ethers from alcohols. Write chemical equations.
9. What are symmetrical and unsymmetrical ethers. Give one example in each case.
10. Write IUPAC name of diethyl ether. How will you obtain it from ethanol ? *(Delhi Board 1990)*
11. How is ethyl alcohol converted into diethyl ether. *(Delhi Board 1994)*
12. Explain, giving a suitable reason :
    (*i*) Ethyl alcohol boils at 351 K while diether ether boils at 308 K.
    (*ii*) The dipole moment of ether (1.18D) is less than water (1.4D).
    (*iii*) The C—O—C bond angle in ethers is greater than H—O—H bond angle though oxygen is sp^3 hybridised in each case.
    (*iv*) Ethers are used as solvents in many organic reactions.
    (*v*) Ethers produce oxonium ion with dil. cold acid.
13. How does anisole react with
    (*i*) HI at 373 K (*ii*) Bromine in CCl_4 (*iii*) conc. HNO_3/H_2SO_4.
14. During distillation of ethers, sometimes a serious accident is likely to occur, why ?
15. How is the presence of peroxides in ethers detected and removed. *(Delhi Board 1992)*
16. What is Williamson's synthesis ? What type of compounds are prepared by this synthesis. Give one example. *(Delhi Board 1994)*
17. How can diethyl ether be prepared from
    (*i*) Grignard's reagent (*ii*) Diazo methane (*iii*) Ethyl iodide.
18. What is IUPAC name of methyl ter-butyl ether ? Write one method each for synthesis and cleavage of ethers. *(Delhi Board 1991)*
19. Write structural formulae of ethyl isopropyl ether.
20. What kind of isomerism is shown by diethyl ether ?
21. Name the starting material required for the preparation of 2-methoxypropane by Williamson's method.
22. Why ethers have a low boiling point ?
23. The C—O—C bond angle in ethers is 110°, why ?
24. Why are ethers in soluble in water, in general. *(Delhi Board 1993)*
25. Diethyl ether does not react with sodium, why ? *(B.I.T. Ranchi 1992)*
26. What products are obtained when ter-butyl methyl ether is treated with HI ?
27. Write equation for the reaction of methyl magnesium iodide with monochloro dimethyl ether.
28. Name the product obtained when THF is heated with HBr at 373 K.

Aldehydes and Ketones

29. What are carbonyl compounds ? How do aldehydes react with :
    (*i*) sodium bisulphite (*ii*) phenyl hydrazine (*iii*) Grignard's reagent.
30. Describe the orbital structure of carbonyl group giving hybrid state of carbon atom.
31. How do you account for the greater reactivity of aldehydes in comparison to ketones ?
32. Give two reactions to distinguish between aldehydes and ketones. *(CBSE 1991)*
33. Arrange the following in increasing order of boiling points :
    (*i*) $C_2H_5—O—C_2H_5$, C_3H_7COOH, C_4H_9OH
    (*ii*) $C_3H_7—CHO$, $CH_3—CO—C_2H_5$, $C_2H_5COOCH_3$, $(CH_3CO)_2O$

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34. Give two chemical properties in which HCHO and CH_3CHO differ.

35. Give a brief account of the following reactions :

(*i*) Crossed aldol condensation (*ii*) Crossed Cannizzaro's reaction

(*iii*) Perkin's reaction (*iv*) Reformatsky reaction

(*v*) Etard's reaction.

36. Distinguish between

(*i*) Benzoic acid and phenol (*ii*) Acetaldehyde and propane. [CBSE (1) 1992]

37. *Account for the following :*

(*i*) During the preparation of ammonia derivatives from aldehydes or ketones, pH of the reaction is carefully controlled.

(*ii*) The boiling points of aldehydes and ketones are lower than the corresponding alcohols and acids.

[CBSE (2) 1991]

(*iii*) Dipole moment of aldehydes and ketones are higher than those of alcohols.

(*iv*) Acetone is highly soluble in water but acetophenone is not.

38. What is the formula of compound which produces DDT by reaction with C_6H_5Cl ?

39. Write equation for the reaction of acetyl chloride with dimethyl cadmium.

40. Name the compound from which pinacol is obtained.

41. What is Tollen's reagent ?

42. Butanal and butanol have different boiling points, why ?

43. What is Benedict's solution ?

44. Name two carbonyl compounds which do not produce crystalline products with sodium bisulphite.

45. Convert toluene to benzaldehyde in one step.

46. How will you obtain acetaldehyde from methyl magnesium iodide in one step ?

47. Name the product obtained when calcium acetate is heated strongly and distilled.

48. What type of carbonyl compounds undergo iodoform reaction ?

49. Name the aldehyde which does not give Fehling solution test. (Pb. Board 1994)

50. Arrange HCHO, CH_3COCH_3, CH_3CHO in order of increasing reactivity towards HCN. (I.I.T. 1990)

51. Name the reagent that can be used to separate a mixture of ethyl alcohol and acetaldehyde.

52. Name a chemical test employed to distinguish formaldehyde from acetaldehyde.

53. What type of aldehydes undergo Cannizzaro's reaction ?

54. Give brief description of the following :

(*i*) Tollen's test (*ii*) Cannizzaro's reaction [CBSE (4) 1992]

(*iii*) Rosenmund's reaction [CBSE (2) 1992] (*iv*) Wolff Kishner reduction

(Delhi Board 1992 : AISB 199)

(*v*) Aldol condensation (CBSE 1992 ; CBSE 1993 ; H.P. Board 1993)

(*vi*) Clemmensen reduction. (H.P. Board 1989 S)

55. Suggest chemical test to distinguish between :

(*i*) 2-Pentanone and 3-pentanone (*ii*) Phenol and benzoic acid.

56. How do the following react ?

(*i*) Acetyl chloride and H_2 in the presence of palladium catalyst

(*ii*) Toluene and acetic anhydride in the presence of chromic oxide

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(*iii*) Acetaldehyde and HCN

(*iv*) Acetyl chloride and toluene in the presence of anhydrous $AlCl_3$

(*v*) Semicarbazide and formaldehyde (*vi*) Ethanol and ethanal

(*vii*) Benzoic acid and thionyl chloride (*viii*) Ethyl benzene and alkaline potassium permanganate.

57. An organic compound C_2H_4O gives red ppt. when warmed with Fehling solution. It also undergoes aldol condensation in the presence of alkali.

(*i*) Write IUPAC name of the compound.

(*ii*) What is the state of hybridisation of carbon atoms in the compound ?

(*iii*) Write balanced equation for reaction. ***(Pb. P.M.T. 1991)***

Acids and Acid Derivatives

58. Acids change the colour of litmus, why ?

59. Carboxylic acids decompose sodium bicarbonate, why ?

60. Give a suitable example of H.V.Z. reaction. ***(Har. Board 1990 S)***

61. How does formic acid react with Tollen's reagent ?

62. Arrange the following in order of increasing acidic strength :

(*a*) $CH_3CH(I)COOH$, $CH_2(Cl)CH_2COOH$, CH_3CH_2COOH

(*b*) $CH_2ClCOOH$, CCl_3COOH, $CHCl_2COOH$

(*c*) $CH_3CH_2CO_2H$, HCOOH, $(CH_3)_2CHCOOH$.

63. How is vinegar obtained from ethyl alcohol ?

64. What kind of isomerism is shown by acids ?

65. What is acylation ?

66. How does acetyl chloride react with phenol ? ***(Har. Board 1990)***

67. What is trans-esterification ?

68. Arrange in order of increasing reactivity

Acetyl chloride, Acetamide, Methyl acetate.

69. What is Hoffmann's Bromamide reaction ?

70. Arrange in the order of ease of hydrolysis

$$CH_3COOC_2H_5,\ CH_3COCl,\ (CH_3CO)_2O,\ CH_3CONH_2.$$ ***(I.I.T. 1986)***

71. How do you account for the fact that :

(*i*) Trichloro acetic acid is stronger acid than chloroacetic acid

(*ii*) α-chloro butyric acid is stronger acid than β-chlorobutyric acid

(*iii*) Acetic acid is stronger acid than phenol

(*iv*) Why do acetyl chloride fumes in air

(*v*) Molecular mass of ethyl acetate is higher than acetic acid but boiling point of ethyl acetate is less than that of acetic acid.

(*vi*) The boiling points of acids are higher than the corresponding alcohols.

(*vii*) Chloroacetic acid is stronger than acetic acid. ***(Pb. Board 1991 ; Delhi Board 1994)***

(*viii*) In the preparation of an ester by the reaction of a carboxylic acid and an alcohol, the ester is distilled as fast as it is formed.

72. An acid on reduction with HI gave propane. What will be the products if sodium salt of the same acid is subjected to

(*i*) sod lime decarboxylation (*ii*) Kolbe's electrolytical decarboxylation.

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73. What is HVZ reaction ? What is the function of P in it ? Give two reactions to describe its utility.

74. Of various acid derivatives, which one is least reactive and which is most reactive ?

75. Explain the following about acetic acid :

(*i*) Its boiling point is higher than that of *n*-propyl alcohol

(*ii*) It is weaker acid than chloroacetic acid and formic acid. ***(A.I. CBSE 1991)***

76. *Account for the following :*

(*i*) Carboxylic acids do not give properties of aldehydes and ketone. ***(Delhi Board 1988)***

(*ii*) The two carbon-oxygen bonds in sodium formate have the same value (1.27 Å). ***(I.I.T. 1988)***

(*iii*) Acetic acid can be halogenated in the presence of red P and Cl_2 but formic acid cannot be halogenated in the same way. ***(I.I.T. 1988)***

(*iv*) Acetic acid is a weaker acid than formic acid. ***(C.B.S.E. 1991)***

77. Compare the strength of following acids :

(*i*) Formic acid (*ii*) Acetic acid (*iii*) Benzoic acid. ***(Delhi Board 1992)***

78. How will you obtain trichloro acetic acid from acetic acid ? ***(CBSE 1989)***

79. Write chemical equations for the following reactions :

(*i*) Decarboxylation of malonic acid ***(Delhi Board 1990)***

(*ii*) Acetic acid is heated with red phosphorus and HI ***(Pb. Board 1994)***

80. Write short notes on the following :

(*i*) Kolbe's electrolytic reaction ***(CBSE 1988 ; Delhi Board 1992, 93)***

(*ii*) Hell-Volhard Zelinsky reaction ***(CBSE 1987 ; Delhi Board 1987)***

(*iii*) Esterification reaction. ***(Pb. Board 1990 S)***

81. Give at least two chemical tests to distinguish between the following pairs of compounds :

(*i*) Phenol and benzoic acid ***(H.P. Board 1992)***

(*ii*) Acetic acid and formic acid ***(Pb. Board 1994)***

(*iii*) Acetic acid and benzoic acid.

82. How is acetic acid obtained from methanol in one step ? ***(Pb. Board 1994)***

83. Account for the following :

(*i*) Acyl chlorides have lower boiling points than corresponding acids ***(A.I.S.B. 1990 S)***

(*ii*) Acetyl chloride fumes in air

(*iii*) Ethyl acetate is more reactive than acetyl chloride

(*iv*) The boiling point of esters are lower than those of corresponding acids.

84. How is acetamide prepared from

(*i*) Acetonitrile (*ii*) Acetyl chloride.

85. Give one method each for the preparation of the following compounds :

(*i*) Ethyl acetate (*ii*) Acetic anhydride (*iii*) Acetamide.

MISCELLANEOUS QUESTIONS/PROBLEMS

86. Give at least two chemical tests to distinguish between the following pairs of compounds :

(*i*) Acetaldehyde and acetone ***(H.P. Board 1990, 92, 94 ; CBSE 1989 ; Delhi Board 1989)***

(*ii*) Acetone and formaldehyde ***(CBSE 1985 S)***

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(*iii*) Ethyl alcohol and acetaldehyde (*CBSE 1986*)

(*iv*) Pentanone-2 and pentanone-3 (*Delhi Board 1988*)

(*v*) $C_6H_5COCH_3$ and $C_6H_5CH_2CHO$ (*Delhi Board 1986*)

(*vi*) Propanal and acetone (*Har. Board 1987*)

87. Write equations for the reaction of

$$HOOC—CH = CH—\underset{\displaystyle OCH_3}{\underset{|}{CH}}—CHO$$

with each of the following reagents :

(*i*) dilute $KMnO_4$ in the presence of alkali (*ii*) a dilute solution of Na_2CO_3

(*iii*) bromine (*iv*) phenyl hydrazine (*v*) Tollen's reagent.

88. How will you obtain the following compounds from acetone ? Write chemical equations also

(*i*) Mesityl oxide (*ii*) Diacetone amine (*iii*) Mesitylene

(*iv*) Phorone (*v*) Diacetonyl alcohol.

86. An ester has a molecular mass of 102. On aqueous hydrolysis, it yields a monobasic acid (A) and an alcohol (B) 0.185 g of acid A requires 25 ml of 0.1 N NaOH. Find out the formula of ester, (A) and (B).

(*Roorkee Ent. 1990*)

87. An organic compound X contains C, H and O elements. X does not react with any of the following :

(*i*) Br_2 (*ii*) Na (*iii*) Schiff's reagent.

On refluxing X with excess of HI, Y is produced. But on hydrolysis with dilute H_2SO_4, X gives Z. Oxidation of Z produces a mono carboxylic acid with molecular mass 60 gm mol^{-1}. Identify X, Y, Z and give sequence of reaction.

(*I.I.T.J.E.E. 1981*)

88. Identify the product A, B, C in the following sequence of reactions

$$[A]\ C_3H_8O \xrightarrow{PCl_5} [B] \xrightarrow{KCN\ (alc.)} C_4H_7N\ [C] \xrightarrow{Hydrolysis} [D] \text{ is 2-Methyl propionic acid } [D]$$

89. An alkene [A] on reductive ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to B. [B] on treatment with Br_2 in the presence of phosphorus yields a compound [C] which on further hydrolysis gives a hydroxy acid [D]. The acid [D] can also be produced from acetone by treatment with HCN followed by subsequent acidic hydrolysis. Identify A, B, C, D.

(*I.I.T.J.E.E. 1982*)

90. An aromatic compound C_7H_8 (A) on nitration gives (B). The reduction product of (B) on treatment with $NaNO_2$ and HCl at 273 K followed by subsequent treatment with CuCl and HCl gives (C). On oxidation (C) gives a compound (D) with formula $C_7H_5O_2Cl$. D is ortho substituted aromatic carboxylic acid. Identify A, B, C, D.

91. A compound A ($C_5H_{11}O$) shows following reactions : (*i*) reacts with acetyl chloride (*ii*) evolved H_2 with sodium and (*iii*) produces dense oily layer with $HCl/ZnCl_2$ immediately. **A** on passing through Al_2O_3 at 350°C gave **B**, which on further reductive ozonolysis gave **C** and **D**. **C** and **D** gave test for carbonyl group but only **C** respond to Fehling test. Give structures of **A, B, C, D.**

(*Roorkee Ent. 1991*)

92. Compound (A) $C_5H_{10}O$ forms a phenylhydrazone and gives a negative Tollen's and iodoform tests. Compound (A) on reduction gives *n*-pentane. Give the structure of compound (A) and explain the reactions.

(*Roorkee 1987*)

93. An unknown compound A, containing 69.77% carbon and 11.63 hydrogen and rest oxygen has a molecular mass of 86. It does not reduce Fehling's solution but forms a bisulphite addition compound and gives a positive iodoform test. What are the possible structures ?

(*I.I.T. 1987*)

94. A hydrocarbon A (molecular formula C_5H_{10}) yields 2-methylbutane on catalytic hydrogenation. (A) adds HBr in accordance with Markownikoff's rule to form a compound (B) which on reaction with silver hydroxide forms an alcohol (C), $C_5H_{12}O$. Alcohol (C) on oxidation gives a ketone (D). Deduce the structure (A), (B), (C) and (D) and show the reactions involved.

(*I.I.T. 1988*)

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95. A ketone (A) which undergoes haloform reaction gives compound (B) on reduction. B on heating with sulphuric acid gives compound C, which forms monozonide D. D on hydrolysis in presence of zinc dust gives only acetaldehyde. Identify A, B, and C. Write down the reactions involved. *(I.I.T. 1989)*

96. An organic compound (A) of molecular weight 140.5 has 68.32% C, 6.4% H and 25.26% Cl. Hydrolysis of (A) with dilute acid gives compound (B), $C_8H_{10}O$. Compound (B) can be oxidized under mild conditions to compound (C), C_8H_8O. Compound (C) forms phenylhydrazone (D) and gives a positive iodoform test. Deduce the structures of compounds (A) to (D) with proper reasoning. *(Roorkee 1990)*

97. An organic compound containing C, H, O exists in two isomeric forms **A** and **B**. 0.108 g of one of the isomers gives on combustion 0.308 g of CO_2 and 0.72 g of H_2O. **A** is insoluble in NaOH and $NaHCO_3$ while **B** is soluble in NaOH. **A** reacts with HI to give compound **C** and **D**. **C** can be separated from **D** by ethanolic solution of $AgNO_3$. **D** is also soluble in NaOH soln. **B** reacts readily with Br_2 water to give **E** having formula $C_7H_5OBr_3$. Identify **A, B, C, D, E** with justification. *(I.I.T.J.E.E. 1991)*

98. Two moles of an ester (**A**) are condensed in the presence of sodium ethoxide to give β-keto ester (**B**) and ethanol. On heating in acidic solution, (**B**) gives ethanol and β-keto acid (**C**). Decarboxylation of **C** gives 3-pentanone. Identify **A, B, C, D**. Name the reaction involved in the conversion of **A** to **B**. *(Roorkee Ent. 1992)*

99. An organic compound (A), C_6H_{10}, on reduction first gives (B), C_6H_{12}, and finally (C), C_6H_{14}. (A) on ozonolysis followed by hydrolysis gives two aldehydes (D), C_2H_4O, and (E), $C_2H_2O_2$. Oxidation of B with acidified $KMnO_4$ gives the acid (F), $C_4H_8O_2$. Determine the structures of the compounds (A) to (F) with proper reasoning. *(Roorkee Ent. 1993)*

100. An organic compound (A), C_7H_8O, is insoluble in aqueous $NaHCO_3$ but soluble in NaOH. (A) on treatment with bromine water rapidly forms compound (B), $C_7H_5OBr_3$

(*i*) Give structures of (A) and (B)

(*ii*) What will be (A), if it, does not dissolve in NaOH but shows reactions given above.

Give your answers with proper reasoning. *(Roorkee Ent. 1993)*

101. An organic halide on reaction with sodium isopropoxide gives a compound A ($C_5H_{12}O$). The compound A on heating with HI produces B and C. C on warming with sodium hypoiodite gives yellow precipitate (compound D) and also on warming with conc. H_2SO_4 at 413 K it gives E which does not react with Na. Predict A, B, C, D, E and write equations for reactions.

102. An alkene (A) on ozonolysis yields acetone and an aldehyde. The aldehyde is easily oxidised to an acid (B). When (B) is treated with Br_2 in the presence of phosphorus, it yields compound (C) which on hydrolysis gives a hydroxy acid (D). This acid can also be obtained from acetone by the reaction with HCN followed by hydrolysis. Identify compounds (A), (B), (C) and (D). *(I.I.T. 1982)*

103. Compound (A) $C_5H_8O_2$ liberated CO_2 on reaction with sodium bicarbonate. It exists in two forms neither of which is optically active. It yields (B) $C_5H_{10}O_2$ on hydrogenation. Compound (B) can be separated into two enantiomorphs. Write the structural formulae for (A) and (B) giving reasons. *(Roorkee 1987)*

104. An organic monobasic acid has 68.9% carbon and 4.8% hydrogen. 0.122 of the acid requires 10 ml of N/10 caustic soda solution for neutralisation. What is the molecular formula of the acid. *(I.S.M. Dhanbad, 1991)*

105. A hydrocarbon (A), C = 90.56% and vapour density 53 was subjected to vigorous oxidation to give a dibasic acid (B). 0.10 g of (B) required 24.1 ml of 0.05 N NaOH for complete neutralization. Nitration of (B) gave a single mononitro derivative. When (B) was heated strongly with sodalime, it gave benzene. Identify (A) and (B) with proper reasoning and also give their structures. *(Roorkee, 1991)*

COMPLETE THE EQUATIONS

Complete the following equations and give the names of important products :

(A.I.S.B. 1985)

1. $HCHO + NH_3 \longrightarrow$

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2. $Ca(CH_3COO)_2 \xrightarrow{Distil}$

3. $CH_3COCH_3 + I_2 \xrightarrow{NaOH}$

4. $C_6H_5COOH + Br_2 \xrightarrow{FeBr_3}$

5. $CH_3CH_2CH_2COOH + Cl_2 \xrightarrow{P} ? \xrightarrow{KOH\ (alc.)} ?$

6. $CH_3COCl \xrightarrow{CH_3NH_2} ?$

7. $C_6H_5CONH_2 + HONO \longrightarrow$

8. $CH_3COCH_3 + HCN \longrightarrow$

(*CBSE 1985*)

9. $CH_3CHO + (CH_2OH)_2 \xrightarrow{H^+}$ (*CBSE 1984*)

10. $CH_3CHO \xrightarrow{Dil.\ NaOH}$ (*CBSE 1988*)

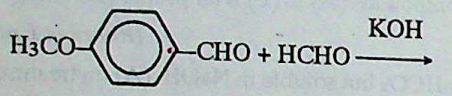
11. $HCHO \xrightarrow[heat]{conc.\ NaOH}$

(*CBSE 1988*)

12. $HCHO + NH_2CONHNH_2 \longrightarrow$

13. $HCHO + RMgX \xrightarrow{H_2O/H^+}$ (*CBSE 1990*)

14. $CH_3COCH_3 + H_2NOH \xrightarrow{HCl}$

15. 

(*I.I.T. 1992*)

Identify X and Y and complete each of the following equations :

16. $CH_3CH_2OH \xrightarrow{K_2Cr_2O_7/H^+} X \xrightarrow[\text{the cal. salt}]{Distill} Y \xrightarrow{Cl_2/NaOH}$ Chloroform

17. $CH_3CHCl_2 \xrightarrow{aq.\ NaOH} X \xrightarrow[\text{Solution}]{Fehling} Y + H_2O + Cu_2O$

18. $CH_3CHO \xrightarrow{Oxidation} X \xrightarrow{PCl_5} Y \xrightarrow{CH_3COONa} (CH_3CO)_2O$

19. $CH_3COCl \xrightarrow{Cd(CH_3)_2} X \xrightarrow{PCl_5} Y$

20. $C_6H_5COOH \xrightarrow[\text{Pyridine}]{SO_2Cl_2} X \xrightarrow[\text{aq. NaOH}]{Y}$ Phenyl benzoate

21. $CH_3CH_2OH \xrightarrow[300°C]{Cu} X \xrightarrow{Dil.\ NaOH} Y$

22. $C_2H_5OH \xrightarrow[C_2H_5I]{Na} X \xrightarrow{Cl_2,\ h\nu} Y$

23. $X \xrightarrow{CH_3I} (CH_3)_2CHOCH_3 \xrightarrow{HI} Y$ (major product)

24. $CH_3CH_2OH \xrightarrow[413\ K]{H_2SO_4} X \xrightarrow{HI\ excess} Y$

25. $C_6H_5OH \xrightarrow[NaOH]{(C_2H_5)_2SO_4} X \xrightarrow{HI} Y$

26. $(CH_3)_3COCH_3 \xrightarrow{HI} X + Y$

27. $CH_3CH_2CHCl_2 \xrightarrow[Boil]{Alkali}$

(*I.I.T.J.E.E. 1992*)

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28. $CH_3CHO \xrightarrow[H_2SO_4]{KMnO_4} X \xrightarrow[P_4]{Cl_2} Y$

29. $CH_3CH_2OH \xrightarrow[575\ K]{Cu} X \xrightarrow[\Delta]{Al(OC_2H_5)_3} Y$

30. $CH_3COOH \xrightarrow{NH_4OH} X \xrightarrow[heat]{P_2O_5} Y$

31. $CH_3CH_2I \xrightarrow[Et_2O]{Mg} X \xrightarrow[(ii)\ H_2O/H^+]{(i)\ CO_2} Y$

32. $HC \equiv CH \xrightarrow{CH_3COOH} X \xrightarrow{heat} CH_3CHO + Y$

33. $CH_3COOH \xrightarrow{Cl_2/P_4} X \xrightarrow[(ii)\ H_2O/H^+]{(i)\ alc.\ KCN} Y$

34. $CH_3COOH \xrightarrow{CH_2 = C = O} X \xrightarrow{C_6H_6} Y$

35. $CH_3CONH_2 \xrightarrow{Br_2/KOH} X \xrightarrow[KOH]{CHCl_3} Y$

36. $CH_3COOH \xrightarrow{SOCl_2} X \xrightarrow[(ii)\ H_2O/H^+]{(i)\ alc.\ KCN} Y.$

WHAT HAPPENS WHEN

State giving equations as to what happens when

1. Sodium acetate is heated with soda lime. ***(Pb. P.M.T. 1991)***
2. Acetylene is bubbled through the very dilute sulphuric acid containing mercuric sulphate.
3. Vapours of 2-propanol are passed over heated copper.
4. Acetone is treated with CH_3MgBr and the product is hydrolysed.
5. 2-Methyl-2-butene is subjected to reductive ozonolysis.
6. Benzyl methyl ketone is allowed to react with ethylene glycol.
7. Ethyl bromide is treated with sodium cyclopentanolate.
8. Anisole is treated with acetic anhydride in the presence of $AlCl_3$.
9. Benzaldehyde is warmed with ethanal in the presence of dilute alkali.
10. Benzoic acid is treated with methanol in H_2SO_4.
11. Benzoyl chloride is heated with acetic acid.
12. Toluene is warmed with chromy chloride.
13. Calcium acetate is heated with sulphuryl chloride.
14. Benzoyl chloride is treated with phosphoryl chloride.
15. Isopropyl bromide is treated with sodium methoxide.
16. Reductive ozonolysis of isobutylene is done.
17. Ethylbenzene is heated with chromyl chloride.
18. Acetylene is treated with acetic acid and the product heated strongly.
19. Formaldehyde is treated with NaOH. ***(Har. Board 1990)***
20. Acetaldehyde is treated with methyl magnesium halide and then hydrolysed. ***(Har. Board 1990)***
21. Acetaldehyde is reacted with $K_2Cr_2O_7$ and H_2SO_4. ***(M.L.N.R. 1992)***
22. Acetaldehyde is kept with a trace of sulphuric acid. ***(Delhi Board 1992 S)***
23. Benzaldehyde is treated with mild oxidizing agents like acidified $KMnO_4$ solution. ***(H.P. Board 1994)***
24. Acetaldehyde is heated with Aluminium ethoxide.

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25. Benzaldehyde is treated with alcoholic solution of KCN.
26. Acetaldehyde reacts with dil NaOH. *(CBSE 1989)*
27. Formaldehyde reacts with RMgX. *(CBSE 1990)*
28. Propion aldehyde is treated with ammoniacal silver nitrate followed by heating with P_2O_5.
29. Acetaldehyde is warmed with chromic acid followed by dry distillation with $Ca(OH)_2$. *(Dhanbad 1992)*
30. Acetone is heated with ethylene glycol and H_2SO_4.

CONVERSIONS

Bring out the following conversions :

Ethers

1. Methyl iodide to methoxyethane.
2. Ethyl iodide to 2-methoxy propane.
3. Isopropyl chloride to 2-ethoxy propane.
4. Iodobenzene to anisole.
5. Ethyl iodide to phenetole.
6. Ethyl alcohol to diethyl ether. *(A.I. CBSE 1993)*

Aldehydes/Ketones

7. Acetyl chloride into acetaldehyde. *(CBSE 1993)*
8. Acetone to ter-butyl alcohol. *(H.P. Board 1993)*
9. Ethanol to acetaldehyde. *(CBSE 1992 S)*
10. Acetic acid to acetaldehyde. *(CBSE 1992 S)*
11. 2-Butanol to butanone. *(Delhi Board 1992)*
12. Toluene to benzaldehyde. *(CBSE 1993)*
13. Propyne to propanone. *(Har. 1992)*
14. Acetic acid to acetone. *(H.P. Board 1992)*
15. Acetylene to acetaldehyde. *(CBSE 1990)*
16. Acetophenone to ethyl benzene. *(Pb. Board 1994)*
17. Acetaldehyde to isopropyl alcohol. *(H.P. Board 1993)*
18. Acetone to pinacol.
19. Formaldehyde to methyl alcohol. *(Delhi Board 1987)*
20. HCHO to urotropine. *(Pb. Board 1994)*
21. Ethanal to 2-Butenal. *(Delhi Board 1993)*
22. Ethyl alcohol to lactic acid.
23. Acetone to diacetone amine.
24. Methanal to ethanal.
25. Acetone to acetylene. *(CBSE 1989)*

Acid and Acid Derivatives

26. Propanoic acid to 3-pentanone.
27. Propanoic acid to propanol. *(Har. Board 1992)*

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28. Toluene to *m*-nitrobenzoic acid. *(I.I.T. 1988)*
29. Ethanoic acid to a mixture of methanoic acid and diphenyl ketone. *(I.I.T. 1990)*
30. Methyl iodide to acetic acid. *(Dhanbad 1992)*
31. Benzamide to aniline. *(Delhi Board 1993)*
32. Acetic acid to acetic anhydride. *(Delhi Board 1993)*
33. Acetyl chloride to acetaldehyde. *(CBSE 1993)*
34. Toluene to benzoyl chloride.
35. Benzamide to phenyl isocyanide.

Miscellaneous

36. Propanoic acid into acetic acid. *(A.I. CBSE 1992)*
37. Acetophenone to ethylbenzene.
38. Acetophenone to benzoic acid. *(CBSE 1992)*
39. Anisole to *o*-nitroanisole.
40. Ethanamide to ethylamine.
41. Ethanamide to methylamine.
42. Acetaldehyde to acetone. *(A.I. CBSE 1992)*
43. Acetone to tertiary butyl alcohol.
44. Ethyl alcohol to vinyl acetate. *(I.I.T.J.E.E. 1989)*
45. Acetic acid to 2-methyl-2-propanol. *(I.I.T.J.E.E. 1989)*
46. Toluene to benzaldehyde. *(CBSE 1992)*
47. Acetaldehyde to ethane. *(CBSE 1992)*
48. Acetone into iodoform. *(CBSE 1992)*
49. Methoxymethane to ethoxyethane.
50. Acetone into chloretone. *(Har. 1992)*
51. Propanonic acid into 3-pentanone. *(Har. 1992)*
52. Phenol to acetophenone. *(I.I.T.J.E.E. 1989)*
53. Ethyl alcohol to malonic acid.
54. Acetic acid to methylamine.
55. Formaldehyde to *n*-butane. *(A.I. CBSE 1991)*
57. How can you prepare the following compounds :
    (*i*) Acetic acid from acetylene.
    (*ii*) Acetic anhydride from acetic acid.
    (*iii*) Ethyl propanoate from propanoic acid and ethanol. *(CBSE 1992)*
    (*iv*) Benzamide from benzoic acid.
    (*v*) Diethyl ether from ethyl iodide.
    (*vi*) Benzaldehyde from benzoyl chloride.
    (*vii*) Acetophenone from benzene. *(CBSE 1992)*
    (*viii*) 2-Propanol from propanone.
    (*ix*) α-Hydroxy-propionic acid from acetaldehyde.
    (*x*) *m*-nitrobenzoic acid from benzoic acid.
    (*xi*) Propanol from propanoic acid.

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FOR THE COMPETITIVE EXAMINATION

MULTIPLE CHOICE QUESTIONS

Select the correct answers from the following questions :

1. What is the correct bond angle in dimethyl ether

(*a*) 109° 28′ (*b*) 110° (*c*) 120° (*d*) 180°.

2. Ethers are isomeric with

(*a*) Carboxylic acids (*b*) Aldehydes (*c*) Alcohols (*d*) Ketones.

3. The reactants used in Williamson's synthesis of ethers are

(*a*) alcohols and aldehydes (*b*) alkyl halides and sodium carboxylate

(*c*) alkyl halides and sodium alkoxide (*d*) any of the above.

4. Isopropyl iodide on reaction with sodium ethoxide shall produce mainly

(*a*) 2-Ethoxypropane (*b*) Ethene (*c*) Propene (*d*) Ethoxyethane.

5. Anisole on reaction with HI forms

(*a*) Phenol and methyl iodide (*b*) Iodobenzene and methanol

(*c*) Benzene and methyl iodide (*d*) Phenol and methanal.

6. On heating sodium ethoxide with dimethyl sulphate the product obtained is

(*a*) Diethyl ether (*b*) Ethyl methyl ether

(*c*) Dimethyl ether (*d*) Sodium sulphate.

7. 2-Methoxy-2-methyl propane on heating with HI shall produce

(*a*) Methyl alcohol and sec-propyl iodide (*b*) Methyl iodide and ter-butyl alcohol

(*c*) Methyl iodide and isobutene (*d*) Methyl alcohol and ter-butyl iodide.

8. Formaldehyde gives methyl alcohol and sodium formate on treating with NaOH. This is a case of

(*a*) oxidation (*b*) reduction

(*c*) neither oxidation nor reduction (*d*) simultaneous oxidation and reduction.

9. Which one of the following represents the correct charge distribution on the carbonyl group ?

(*a*) $\overset{\delta+}{>}C=\overset{\delta-}{O}$ (*b*) $\overset{\delta-}{>}C=\overset{\delta+}{O}$ (*c*) $\overset{+1}{>}C=\overset{-1}{O}$ (*d*) $\overset{-1}{>}C=\overset{+1}{O}$.

10. Which one of the following products is obtained when acetaldehyde reacts with a dil. alkali ?

(*a*) $CH_3CH_2CH_2OH$ (*b*) $CH_3CHOHCH_2CHO$ (*c*) CH_3COCH_3 (*d*) CH_3COOH.

11. Which compound is obtained when formaldehyde reacts with ammonia ?

(*a*) Formamide (*b*) Methylamine (*c*) Hexamethylene tetramine (*d*) Formaline.

12. Which of the following is the strongest acid ?

(*a*) Formic acid (*b*) Acetic acid (*c*) Propionic acid (*d*) *n*-Butyric acid.

13. Which of the following is the strongest acid ?

(*a*) Acetic acid (*b*) Phenol (*c*) Methyl alcohol (*d*) Water.

14. Which of the following has highest solubility in water ?

(*a*) Acetic acid (*b*) Propionic acid (*c*) *n*-Butyric acid (*d*) Pentanoic acid.

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15. Which of the following cannot reduce Fehling's solution ?
(*a*) Formic acid (*b*) Acetic acid (*c*) Formaldehyde (*d*) Acetaldehyde.
(B.I.T.S. Ranchi 1992)

16. Which of the following acids does not form anhydride ?
(*a*) Formic acid (*b*) Acetic acid (*c*) Propionic acid (*d*) *n*-butyric acid.

17. The acid which does not contain —COOH group is
(*a*) Ethanoic acid (*b*) Lactic acid (*c*) Picric acid (*d*) Palmitic acid.
(I.I.T. Screening 1991)

18. Trans-esterification is a reaction between
(*a*) two ester molecules (*b*) alcohol and carboxylic acid
(*c*) alcohol and ether (*d*) alcohol and ester.

19. Acetone on heating with ammonia produces
(*a*) Acetaldimine (*b*) Diacetone alcohol
(*c*) Diacetonamine (*d*) Hydrobenzamide.

20. Methyl ketones are usually characterised through
(*a*) Tollen's reagent (*b*) Iodoform test
(*c*) Schiff's test (*d*) Benedict solution test. ***(M.L.N.R. 1992)***

21. Which of the following reagents can be used to prepare ketone from acid chloride ?
(*a*) Grignard's reagent (*b*) $LiAlH_4$
(*c*) Dimethyl cadmium (*d*) Cadmium chloride.

22. HVZ reaction is used to prepare
(*a*) β-haloacid (*b*) α-haloacid
(*c*) α, β-unsaturated acid (*d*) None of these.

23. An alkene C_7H_{14} on reductive ozonolysis gives an aldehyde with formula C_3H_6O and a ketone. The ketone is
(*a*) 2-butanone (*b*) 2-pentanone
(*c*) 3-pentanone (*d*) propanone.

24. Acetaldol is a condensation product of
(*a*) two molecules of ethanal (*b*) two molecules of propanone
(*c*) ethanal and methanal (*d*) ethanal and propanone.

25. The enolic form of acetone contains
(*a*) 9σ bonds, 1π bond, 2 lone pairs (*b*) 8σ bonds, 2π bonds, 1 lone pairs
(*c*) 10σ bonds, 1π bond, 2 lone pairs (*d*) 9σ bonds, 2π bonds, 1 lone pairs.
(I.I.T.J.E.E. 1990)

26. Chlorination of toluene in the presence of light and heat followed by treatment with aqueous NaOH gives
(*a*) *o*-Cresol (*b*) *p*-Cresol
(*c*) 2, 4-Dihydroxytoluene (*d*) Benzyl alcohol. ***(I.I.T.J.E.E. 1990)***

27. Hydrogenation of benzoyl chloride in the presence of Pd supported on $BaSO_4$ gives
(*a*) Benzyl alcohol (*b*) Benzaldehyde
(*c*) Benzoic acid (*d*) Phenol. ***(I.I.T.J.E.E. 1992)***

28. $(CH_3)_2C = CHCOCH_3$ can be oxidised to $(CH_3)_2C = CHCOOH$ by
(*a*) Chromic acid (*b*) NaOI
(*c*) Cu at 575 K (*d*) $KMnO_4$. ***(C.B.S.E. 1993)***

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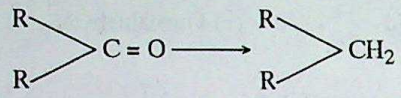
29. Which of the following reactions cannot be used for the reduction of



(*a*) Clemmensen reaction (*b*) Wolff-Kishner reaction
(*c*) Wurtz reaction (*d*) HI and red phosphorus. (*Roorkee, 1993*)

30. Benzaldehyde can be prepared by the hydrolysis of
(*a*) Benzyl chloride (*b*) Benzal chloride
(*c*) Benzotrichloride (*d*) Benzo nitrite. (*C.E.E.T., 1994*)

31. In the reaction, $CH_3COOH \xrightarrow{P_4, Cl_2} A \xrightarrow{NH_3 \text{ (excess)}} B$, the product B is
(*a*) Acetamide (*b*) Glycine
(*c*) Ammonium acetate (*d*) Methane.

32. Benzamide on heating with bromine and caustic alkali gives
(*a*) Benzene (*b*) Methyl amino and benzene
(*c*) Aniline (*d*) *m*-Bromo benzaldehyde.

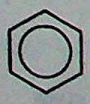
33. The reaction, $C_6H_5COCl + H_2 \xrightarrow[BaSO_4]{Pd} C_6H_5CHO + HCl$, is called
(*a*) Rosenmund's reaction (*b*) Sand meyer's reaction
(*c*) HVZ reaction (*d*) Cannizaro's reaction.

34. The reaction, $CH_3CN \xrightarrow[EtOH]{Na} X \xrightarrow{HNO_2} Y \xrightarrow[\text{reagent}]{\text{Tollen's}} Z$, Z is
(*a*) CH_3CHO (*b*) CH_3CH_2NHOH
(*c*) CH_3CH_2COOH (*d*) CH_3COOH.

35. The weakest acid amongst the following is
(*a*) $ClCH_2COOH$ (*b*) FCH_2CH_2COOH
(*c*) HCOOH (*d*) $CH_2(I)COOH$.

36. Phenol and benzoic acid can be distinguished by reaction with
(*a*) aq. NaOH (*b*) aq. $NaHCO_3$
(*c*) neutral $FeCl_3$ (*d*) aq. NH_3.

37. The carboxylic acid that does not undergo HVZ reaction is
(*a*) CH_3COOH (*b*) $(CH_3)_2CHCOOH$
(*c*) $CH_3CH_2CH_2CH_2COOH$ (*d*) $(CH_3)_3C\ COOH$.

38. In the reaction,  $+ CH_3COOCOCH_3 \xrightarrow[AlCl_3]{\text{anhy.}} X$, X is
(*a*) Phenyl acetate (*b*) Acetophenone
(*c*) Benzoic acid (*d*) Benzo-phenone.

39. The correct order of reactivity is
(*a*) $CH_3COCl > CH_3COOH_2H_5 > CH_3CONH_2$ (*b*) $CH_3COOC_2H_5 > CH_3COCl > CH_3CONH_2$
(*c*) $CH_3CONH_2 > CH_3COCl > CH_3COOC_2H_5$ (*d*) $CH_3COCl > CH_3CONH_2 > CH_3COOC_2H_5$.

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40. In the reaction, $CH_3COOH \xrightarrow{P_4, Cl_2} X \xrightarrow[(ii)\ \text{Dil. HCl}]{(i)\ \text{KCN}} Y$, Y is

(*a*) Malonic acid (*b*) Propionic acid
(*c*) Oxalic acid (*d*) Cyanoacetic acid.

FILL IN THE BLANKS

Fill in the blanks with appropriate item :

1. Acetic acid forms ..... with NH_3 which on heating gives .....
2. Sodalime decarboxylation of sodium propionate produces .....
3. Ethanamide on heating with P_2O_5 gives .....
4. Carbonation of Grignard's reagent involves reaction of ..... with .....
5. Trimethyl acetic acid is ..... than trichloro acetic acid.
6. $C_nH_{2n}O$ represents the general formula of .....
7. The C—O cleavage of ethers can be caused by .....
8. A 40% solution of formaldehyde in water is known as .....
9. The hybrid state of carbon atom in carbonyl group is .....
10. The addition reactions of aldehydes and ketones are initiated by ..... attack on carbonyl carbon.
11. The reaction of acetic anhydride with $LiAlH_4$ followed by subsequent acidic hydrolysis produces .....
12. Alkaline hydrolysis of esters is called .....
13. The Hoffmann bromamide reaction involves the treatment of amides with .....
14. Aliphatic ethers are purified by shaking with ferrous salts of remove ..... which are formed on prolonged standing in contact with air. ***(I.I.T.J.E.E. 1992)***
15. Ethers behave as weakly ..... substances because of the presence of ..... of electrons on the oxygen atom.
16. Fehling 'A' consists of an aqueous solution of $CuSO_4$ while Fehling 'B' consists of an alkaline solution of ..... ***(I.I.T. 1990)***
17. Ethanol vapour is passed over heated copper and the product is treated with aq. NaOH. The product is ..... ***(I.I.T. 1990)***
18. Addition of water to acetylenic compound is catalysed by ..... and ..... ***(I.I.T. 1993)***
19. The IUPAC name of succinic acid is ..... ***(I.I.T. 1993)***
20. Trimer of acetaldehyde is named as .....

TRUE FALSE STATEMENTS

Pick up the True or False statement out of the following :

1. Aldehydes are more easily oxidised than ketones.
2. Fehling solution test can be given by HCOOH but not by other acids.
3. Formaldehyde reacts with ammonia to give Hexamethylene tetramine.
4. Esters cannot be prepared by the oxidation of carboxylic acids.

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5. Acyl chloride on reacting with acid anhydride give esters.
6. Alkyl cyanides can be considered as anhydrides of primary alkanamides.
7. Cannizzaro's reaction can be given by acetaldehyde.
8. Iodoform test can be shown positive by acetaldehyde as well as propionaldehyde.
9. Formic acid is weaker than acetic acid.. *(B.I.T. Ranchi 1992)*
10. Acetaldehyde can be prepared by distillation of calcium acetate. *(B.I.T.S. Ranchi 1992)*
11. Coordination complexes of ethers with Lewis acids are called etherates.
12. Benzaldehyde on heating with ethanolic solution of KCN produces benzonitrile.
13. Two molecules of ethyl acetate in presence of strong base sodium ethoxide produce ethyl acetoacetate.
14. Toluene on heating with chromyl chloride in CCl_4 produces benzoic acid.
15. Benzamide on heating with a caustic potash solution of bromine produced aniline.
16. In Perkin's reaction benzaldehyde is heated with malonic acid and HCl to produce cinnamic acid.

MATCHING TYPE QUESTIONS

Each entry in Column X is some way related to entry in Column Y. Match appropriately.

1. Match the functional group with the reagent with which it can react

X	Y
1. —COOH	1. Tollen's reagent
2. —CHO	2. Sodium bisulphite
3. $CH_3-\overset{\overset{O}{\|}}{C}-$	3. Sodium bicarbonate
4. $-\overset{\overset{O}{\|}}{C}-$	4. Sodium hypo iodite
5. $-COOCH_3$	5. Sodium hydroxide

2.

X	Y
1. Clemmenson reduction	1. α, β-unsaturated compound
2. Cannizaro's reaction	2. red brown precipitate
3. Aldol condensation	3. aldehyde + Zn—Hg/HCl
4. Fehling solution	4. aldehydes containing no α-hydrogen
5. Claisen-Schmidt reaction	5. carbonyl compounds having α-hydrogen

3.

X	Y
1. H.V.Z. reaction	1. $ZnCl_2$
2. Formic acid	2. potassium salt of monocarboxylic acid
3. —COOH group	3. replacement of α-hydrogen by halogen
4. Kolbe's electrolytic reaction	4. $H_2 + CO_2$
5. Carboxylic acid + alcohol	5. deactivating

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HINTS/ANSWERS

REVIEW PROBLEMS

8.9. By reaction of $CH_3\underset{\underset{CH}{|}}{C}H\overset{-}{O}\overset{+}{N}a$ with C_2H_5I.

8.10. (*i*) $CH_3CH = CH_2 + NaCl + C_2H_5OH$ (*ii*) $CH_3CH_2OCH_3 + N_2$
(*iii*) $C_6H_5OCH_3 + Na^+Cl^-$ (*iv*) $CH_3COOCH_3 + CH_3Cl$ (*v*) $(CH_3)_2C = CH_2$

8.14. (*i*) 3-Methyl hexanal (*ii*) 5-Chloro-3-ethyl-2-pentanone
(*iii*) 3-Bromomethyl benzaldehyde (*iv*) 3-Phenyl butanal
(*v*) 2, 3-Dimethyl-3-pentanone

8.15. (*i*) 3-Methyl butanal ; isobutyraldehyde (*ii*) 3-Hydroxy butanal ; *r*-Hydroxy butyraldehyde
(*iii*) 4-Penten-2-one ; Allyl methyl ketone (*iv*) 2-Buten-1-al ; Crotonaldehyde
(*v*) 3-Phenyl-2-propen-1-al ; Cinnamaldehyde

8.16. It gives three isomers, Butyraldehyde, iso-Butyraldehyde, 2-Butanone

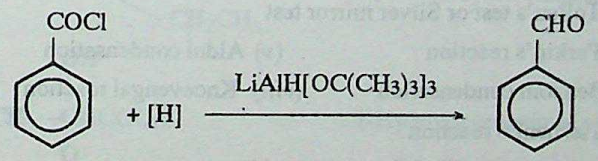
8.17. (*i*) Functional (*ii*) Chain (*iii*) tautomerism

8.18. (*i*) 2-Hydroxy benzaldehyde (*ii*) 2, 4-Pentanedione (*iii*) 3-Buten-2-one
(*iv*) Phenyl acetophenone (*v*) 3-Phenyl-2-propenal

8.24. The acid X is, Isobutyric acid

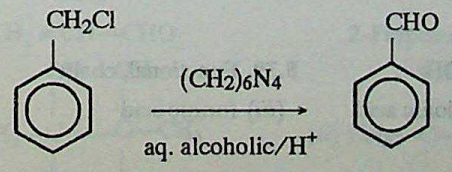
8.25. (*i*) $CH_3CH_2—\underset{\underset{CH_3}{|}}{C} = \underset{\underset{CH_3}{|}}{C}HCH_2CH_3$ (*ii*) $CH_3—\overset{\overset{CH_3}{|}}{C}H—CH = CH—\overset{\overset{CH_3}{|}}{C}H—CH_3$
(*iii*) $CH_3CH = (CH_3)_2$ (*iv*) $H_2C = CH—CH_2CH_3$

8.26. (*i*) $CH_3CH_2OH + \frac{1}{2}O_2\,(air) \longrightarrow CH_3CHO$

(*ii*) 

(*iii*) $CH_3—\overset{\overset{Cl}{/}}{\underset{\underset{Cl}{\backslash}}{C}}—CH_3 + 2KOH(aq) \longrightarrow CH_3—\overset{\overset{O}{\|}}{C}—CH_3 + 2KCl + H_2O$

(*iv*) $CH_3MgI + HC \equiv N \longrightarrow CH_3CH = NMgI \xrightarrow{H_2O/H^+} CH_3CHO + NH_4^+ + Mg\begin{cases}OH\\I\end{cases}$

(*v*) 

(This reaction is known as Sommelet's reaction)

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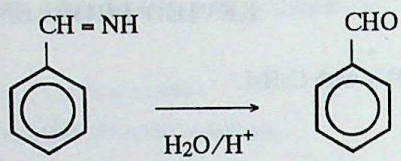
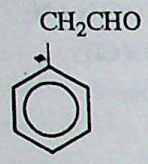
8.27. (*i*) A = $CH_3—\overset{CH_3}{\overset{|}{C}} = CH—CH_3$; B = $CH_3—\overset{O}{\overset{\|}{C}}—CH_3$ and CH_3CHO

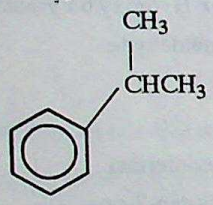
(*ii*) $C_6H_{13}CHO$ (*iii*) A = CH_3COOH ; B = $(CH_3COO)_2Ca$

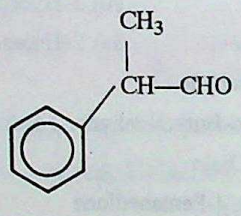
(*iv*) A = Cl—CH = NH ; B = 

(*v*) A = 

(*vi*) A = $(CH_3CH = CH)_3$— B ; B = CH_3CH_2CHO

(*vii*) A = $CH_3C \equiv N$; B = $CH_3CH = NH\ HCl$

(*viii*) A = 

; B = 

(*ix*) A = $HC \equiv CH$; B = CH_3CHO (*x*) A = $CH_3—\overset{CH_3}{\overset{|}{CH}}—CN$; B = $CH_3—\overset{CH_3}{\overset{|}{CH}}—CHO$

8.34. (*i*) $CH_3CH_2\overset{OH}{\overset{|}{C}}HCH_3$ (*ii*) CH_3COOH (*iii*) $CH_3—\overset{CH_3}{\overset{|}{C}} = NH—C_6H_5$

(*iv*) $CH_3—\overset{OH}{\overset{|}{C}}HCH_2COOC_2H_5$ (This reaction is known as *Reformatsky reaction*)

(*v*) $C_6H_5COCH_2Cl$ (Phenacyl chloride)

8.35. (*i*) Cannizaro's reaction (*ii*) Tollen's test or Silver mirror test
(*iii*) Wolff Kishner reduction (*iv*) Perkin's reaction (*v*) Aldol condensation
(*vi*) Gattermann Koch Synthesis (*vii*) Benzoin condensation (*viii*) Knoevengal reaction
(*ix*) Crossed aldol condensation (*x*) Tischenko reaction

8.36. (*i*) 2-Butenoic acid (*ii*) 2-Propenoic acid
(*iii*) 3-Nitro benzoic acid (*iv*) 2, 2-Dimethyl propanoic acid

8.37. (*i*) $C_6H_5CH_2COOH$ (*ii*) $(CH_3)_2CHCH_2COOH$
(*iii*) $HOOC(CH_2)_4COOH$ (*iv*) $\begin{array}{l} CH_2\ COOH \\ | \\ CH_2\ COOH \end{array}$

8.38. (*i*) CH_3CH_2COOH ; CH_3COOCH_3 ; $CH_3—\overset{O}{\overset{\|}{C}}—CH_2OH$

8.39. Functional, chain

8.48. (*i*) trichloroacetic acid (*ii*) α-chloro propionic acid (*iii*) formic acid
(*iv*) *m*-hydroxy benzoic acid (*v*) Benzoic acid.

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8.50. $CH_3-\overset{\overset{O}{\|}}{C}-COOH$ (2-Keto propanoic acid), the optically active acid obtained from it is Lactic acid (2-hydroxy propanoic acid)

NOMENCLATURE

1. 2-Ethoxy propane
2. Methoxy ethene
3. 1, 1-Dimethoxy propane
4. 1-Ethoxy-2-methoxy ethane
5. 1-Ethoxy-2-methyl propane
6. 1-Methoxy-2-phenyl propane
7. 3-Methyl-2-butanone
8. 3-Ethyl hexanal
9. 5-chloro-3-ethyl-2-pentanone
10. 3-Nitro benzaldehyde
11. 2-(2′-Bromo phenyl) ethanal
12. 4-Hydroxy-2-methyl benzaldehyde
13. 4-Methoxy benzaldehyde
14. 4-Hydroxy-4-methyl-2-pentanone
15. 2, 3-Butanedione
16. 2-Butenal
17. 3-Methyl butanal
18. 2, 4-Dimethyl-2-pentanone
19. 2, 3-Dimethyl butanal
20. 1-chloro-5-methyl-2-hexanone
21. 2-Phenyl ethanal
22. Ethanedioic acid
23. 3-Methyl butanoic acid
24. 2-chloro propanoyl chloride
25. Ethyl-2-bromo-3-phenyl propanoate
26. Benzoic anhydride
27. N-Ethyl-N-methyl methanamide
28. 2-Methyl propanamide
29. 2, 3-Dihydroxy butanoic acid
30. 2-Chloro phenyl propanoate
31. N, N-Dimethyl benzamide
32. 3-keto butanoic acid
33. 2-Oxo ethanoic acid
34. 2-Hydroxy propanoic acid
35. 4-Nitro benzoyl chloride
36. Ethyl-2- methyl butanoate

36. (*i*) $CH_3-\overset{\overset{CH_3}{|}}{CH}\,O\,\overset{\overset{CH_3}{|}}{CH}\,CH_3$ 2-(2′-propoxy) propane

(*ii*) $H-\overset{\overset{O}{\|}}{C}-N\begin{matrix}CH_2CH_3\\CH_2CH_3\end{matrix}$ N, N-Diethylmethanamide

(*iii*) $CH_3-\overset{\overset{OH}{|}}{CH}COOH$ 2-Hydroxy propanoic acid

(*iv*) $CH_3-\overset{\overset{O}{\|}}{C}-COOH$ 2-Keto propanoic acid

(*v*) $CH_3-\underset{\underset{CH_3}{|}}{CH}-\overset{\overset{O}{\|}}{C}-CH_3$ 3-Methyl-2-butanone

(*vi*) $CH_2=CH-CHO$ 2-Propenal

37. (*i*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-CH_3$ (*ii*) $CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\overset{\overset{O}{\|}}{C}-CH_3$ (*iii*) $CH_3(CH_2)_3COOH$

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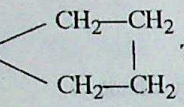
(*iv*) CH_3CONH_2 (*v*) $CH_2(COOH)_2$ (*vi*) $\begin{array}{l} CH_2COOH \\ | \\ CH_2COOH \end{array}$

DESCRIPTIVE QUESTIONS

2. (*iv*)  Tetra hydrofuran

6. (*iii*) Cleavage of phenyl-oxygen bond does not occur it acquires double bond character due to resonance.

19. $CH_3—\overset{CH_3}{\overset{|}{C}}HOC_2H_5$

20. metamerism

21. Methyl iodide and sodium isopropoxide

22. Due to weak dipole-dipole interaction

23. Due to steric repulsions of the bulky alkyl groups

24. lack of effective H-bonding

25. It is because it does not have replaceable hydrogen atom like alcohols

26. $(CH_3)_3C—I$ and CH_3OH

38. Cl_3CCHO (Chloral)

40. acetone by reaction with $Mg\text{-}Hg/H_2O$

41. Ammoniacal solution of silver nitrate

42. Butanol has H-bonding as a result of which its b. pt. is more

43. Aqueous alkaline solution of $CuSO_4$ contain citrate ions

44. Diethyl ketone and aceto phenone

45. $C_6H_5CH_3 \xrightarrow{CrO_2Cl_2} C_6H_5CHO$ (Etard's reaction)

46. $CH_3MgI + HC(=O)—OC_2H_5 \longrightarrow CH_3CHO + Mg(OC_2H_5)I$

47. acetone

49. Benzaldehyde

50. $CH_3COCH_3 < CH_3CHO < HCHO$

51. sodium bisulphite

52. Iodoform test

53. Aldehydes which do not contain α- hydrogen

57. (*i*) Ethanal, (*ii*) sp^2 and sp^3

58. Because acids furnish a good concentration of H^+ ions in solution

59. It is because carboxylic acids are stronger acids ($Ka = 10^{-5}$) than.

60. Carbonic acid ($Ka = 10^{-7}$)

61. $HCOOH + 2[Ag(NH_3)_2]OH \longrightarrow CO_2 + 2H_2O + 2Ag + 4NH_3$

62. (*a*) $CH_3CH_2COOH < CH_2(Cl)CH_2COOH < CH_3CH(I)COOH$
(*b*) $CH_2ClCOOH < CHCl_2COOH < CCl_3COOH$
(*c*) $(CH_3)_2CHCOOH < CH_3CH_2COOH < HCOOH$

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68. Acetamide < methyl acetate < acetyl chloride

70. $CH_3CONH_2 < CH_3COOC_2H_5 < (CH_3CO)_2O < CH_3COCl$

72. The acid is CH_3CH_2COOH

(*i*) CH_3CH_3 is produced (*ii*) $C_2H_5—C_2H_5$ is produced

77. $HCOOH > C_6H_5COOH > HCOOH$

86. Ester is $CH_3CH_2—\overset{O}{\overset{\|}{C}}—OC_2H_5$; A is CH_3CH_2COOH, B is C_2H_5OH

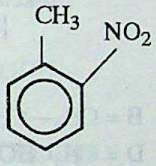
87. X is $C_2H_5OC_2H_5$; Y is C_2H_5I ; Z is C_2H_5OH ; monocarboxylic acid is CH_3COOH.

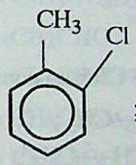
88. A is propan-2-ol ; B is 2-chloropropane ; C is 2-methylpropanenitrile.

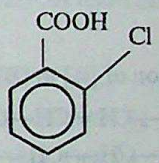
89. A is $CH_3—\underset{\underset{CH_3}{|}}{C} = CH—\overset{\overset{CH_3}{|}}{CH}—CH_3$; B is $CH_3—\overset{\overset{CH_3}{|}}{CH}—COOH$

C is $CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{Br}{|}}{C}}—COOH$; D is $CH_3—\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}—COOH$

90. A is

; B is 

; C is 

; D is 

91. A is $CH_3—\underset{\underset{OH}{|}}{\overset{\overset{CH_3}{|}}{C}}—CH_2CH_3$; B is $CH_3—\overset{\overset{CH_3}{|}}{C} = CHCH_3$; C is $CH_3—\underset{\underset{H}{|}}{C} = O$; D is $CH_3\underset{\underset{CH_3}{|}}{C} = O$

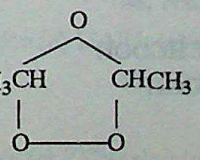
92. $CH_3CH_2COCH_2CH_3$ (3-Pentanone)

93. The possible structures of A are

$CH_3COCH_2CH_2CH_3$ (2-*Pentanone*) and $CH_3COCH(CH_3)_2$ (3-Methyl-2-butanone)

94. A is $(CH_3)_2CHCH = CH_2$; B is $(CH_3)_2CH\overset{\overset{Br}{|}}{C}HCH_3$; C is $(CH_3)_2\underset{\underset{OH}{|}}{C}HCH_3$; D $(CH_3)_2CH\underset{\underset{O}{\|}}{C}CH_3$

95. A is $CH_3COCH_2CH_3$ and B is $CH_3\overset{\overset{OH}{|}}{C}HCH_2CH_3$

C is $CH_3CH = CHCH_3$ and D is 

96. A is $C_6H_5\overset{\overset{Cl}{|}}{C}HCH_3$; B is $C_6H_5\overset{\overset{OH}{|}}{C}HCH_3$; C is $C_6H_5COCH_3$; D is $C_6H_5—\overset{\overset{CH_3}{|}}{C} = NHC_6H_5$

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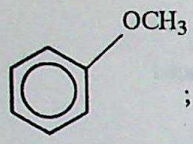
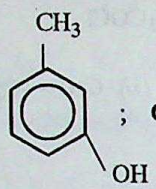
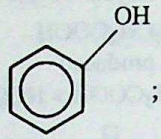
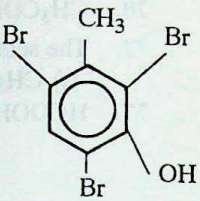
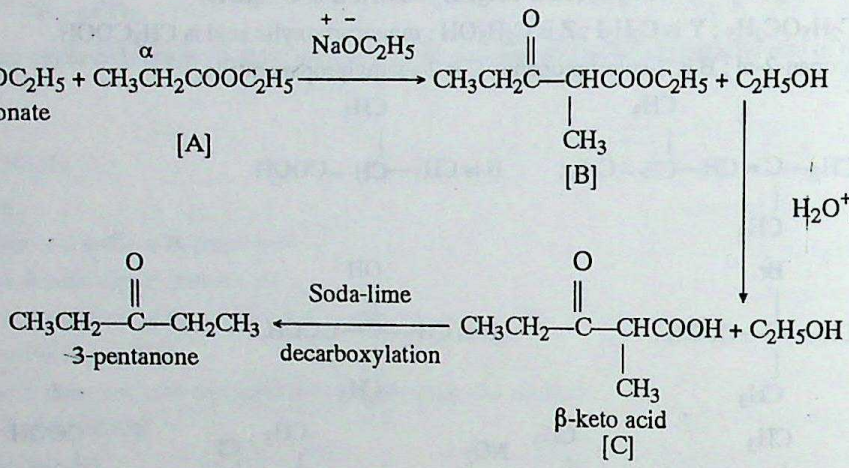
97. Empirical formula : C_7H_8O

A is 

; B is 

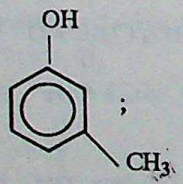
; C is CH_3I ; D is 

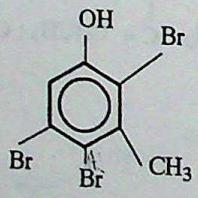
; E is 

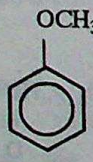
98.


Conversion of **[A]** to **[B]** refers to **Claisen condensation.**

99. A = $CH_3—CH = CH—CH = CH—CH_3$; B = $CH_3—CH = CH—CH_2—CH_2—CH_3$
C = $CH_3—CH_2—CH_2—CH_2—CH_2—CH_3$; D = CH_3CHO
E = $OHC—CHO$; F = $CH_3—CH_2—CH_2—COOH$

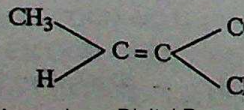
100. (*i*) (A) is 

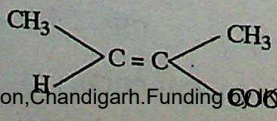
; (B) is 

(*ii*) (A) is 

101. A is $CH_3CH_2—O—CH(CH_3)—CH_3$; B is CH_3CH_2I ; C is $CH_3—CH(OH)—CH_3$; D is CHI_3 (Iodoform) ;
E is $CH_3CH = CH_2$

102. A is $(CH_3)_2C = CH—CH(CH_3)_2$; B is $(CH_3)_2CHCOOH$
C is $(CH_3)_2C(Br)—COOH$; D is $(CH_3)_2C(OH)—COOH$

103. A can be 

and 

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B is $CH_3—CH_2—*C(CH_3)(H)—COOH$ which has a chiral structure and exhibit enantiomerism.

104. $C_7H_6O_2$.

105. A is CH_3–C$_6$H$_4$–CH_3 (*p*-xylene) ; B is HOOC–C$_6$H$_4$–COOH Terephthalic acid.

COMPLETE THE EQUATIONS

For Questions 1—15, refer to the chemical properties of ethers aldehydes/ketons, acids and acid derivatives.

16. X is CH_3COOH, Y is $(CH_3)_2C = O$

17. X is CH_3CHO, Y is CH_3COOH

18. X is CH_3COOH, Y is CH_3COCl

19. X is CH_3COCH_3, Y is $CH_3CCl_2CH_3$

20. X is C_6H_5COCl, Y is phenol

21. X is CH_3CHO, Y is $CH_3CH(OH)CH_2CHO$

22. X = $(C_2H_5)_2O$; Y = $(C_2Cl_5)_2O$

23. X = $(CH_3)_2CH—\overset{-}{O}\overset{+}{N}a$; Y = $(CH_3)_2CHOH$ and CH_3I

24. X = $(C_2H_5)_2O$; Y = C_2H_5I

25. X = $C_6H_5OC_2H_5$; Y = C_6H_5OH and C_2H_5I

26. X = $(CH_3)_3CI$; Y = CH_3OH

27. CH_3CH_2CHO

28. X = CH_3COOH ; Y = $CH_2(Cl)COOH$

29. X = CH_3CHO ; Y = $CH_3COOC_2H_5$

30. X = CH_3COONH_4 ; Y = CH_3CN

31. X = CH_3CH_2MgI ; Y = CH_3CH_2COOH

32. X = $CH_3CH(OOCCH_3)_2$; Y = $(CH_3CO)_2O$

33. X = $CH_2ClCOOH$; Y = $CH_2(COOH)_2$

36. X = CH_3COCl ; Y = $CH_3CH(OH)COOH$

34. X = $(CH_3CO)_2O$; Y = C$_6$H$_4$–$COCH_3$

35. X = CH_3NH_2 ; Y = $CH_3N \rightleftharpoons C$

MISCELLANEOUS CONVERSIONS

Hint. Carry out the following steps :

36. (*a*) NH_3, Heat (*b*) Br_2/KOH (*c*) HNO_2 (*d*) oxidation

37. Clemensen's reduction

38. Oxidation

39. Nitration

40. reduction

42. (*a*) Oxidation ; (*b*) PCl_5 ; (*c*) $(CH_3)_2Cd$

43. (*a*) CH_3MgI ; (*b*) Hydrolysis

44. (*a*) H_2SO_4/440 K ; (*b*) Br_2/CCl_4 ; (*c*) KOH (alc.) ; (*d*) CH_3COOH

45. (*a*) PCl_5 ; (*b*) $Cd(CH_3)_2$; (*c*) CH_3MgI, H_2O

46. Etard's reaction

47. reduction with HI/P

48. $NaOH/I_2$

49. (*a*) HI (excess) (*b*) KCN (alc.) (*c*) oxidation (*d*) $LiAlH_4$ (*e*) H_2SO_4/410 K

50. $CHCl_3$

51. (*a*) $Ca(OH)_2$; (*b*) Distill

52. (*a*) Zn dust ; (*b*) $CH_3COCl/AlCl_3$

53. (*a*) Oxidation (*b*) HVZ reaction with Cl_2/P (*c*) KCN (alc.) (*d*) Hydrolysis

54. (*a*) NH_3, Heat ; (*b*) KOH/Br_2

55. (*a*) CH_3MgI, H_2O ; (*b*) Reduction with HI.

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MULTIPLE CHOICE QUESTIONS

1. (*b*)	2. (*c*)	3. (*c*)	4. (*c*)	5. (*a*)	6. (*b*)
7. (*d*)	8. (*d*)	9. *a*)	10. (*b*)	11. (*c*)	12. (*a*)
13. (*a*)	14. (*a*)	15. (*b*)	16. (*a*)	17. (*c*)	18. (*d*)
19. (*c*)	20. (*b*)	21. (*c*)	22. (*b*)	23. (*a*)	24. (*a*)
25. (*a*)	26. (*d*)	27. (*b*)	28. (*b*)	29. (*c*)	30. (*b*)
31. (*b*)	32. (*c*)	33. (*a*)	34. (*d*)	35. (*b*)	36. (*b*)
37. (*d*)	38. (*b*)	39. (*a*)	40. (*a*).		

FILL IN THE BLANKS

1. Ammonium acetate, acetamide
2. Ethane
3. Ethanenitrile
4. CO_2 with Grignard's reagent
5. Weaker acid
6. aldehydes and ketones
7. HX, H_2SO_4 or PCl_5
8. formalin
9. sp^2
10. nucleophilic
11. ethanol
12. saponification
13. Br_2/KOH
14. etherperoxide
15. basic, lone pair
16. Rochelle salt
17. Aldol
18. dil H_2SO_4, $HgSO_4$
19. Butanedioic acid
20. para aldehyde.

TRUE FALSE STATEMENTS

1. True	2. True	3. True	4. True	5. True	6. True
7. False	8. False	9. False	10. True	11. True	12. False
13. True	14. False	15. True	16. False.		

MATCHING TYPE QUESTIONS

1. 1-3, 2-1, 3-4, 4-2, 5-5
2. 1-3, 2-4, 3-5, 4-2, 5-1
3. 1-3, 2-4, 3-5, 4-2, 5-1

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9

Organic Chemistry Based on Functional Groups—III

(Cyanides, Isocyanides, Nitro Compounds and Amines)

LEARNING OBJECTIVES

In this, Unit, we shall learn

— *to name cyanides, isocyanides, nitro compounds and amines ;*

— *different methods for preparation of cyanides, isocyanides, nitro and amino compounds ;*

— *to correlate the physical properties of nitrogen containing compounds with their structures ;*

— *the chemical properties and reactions of nitrogen containing compounds in terms of their structures ;*

— *the importance of aryl diazonium salts in the preparation of carbon compounds ;*

— *the basis for qualitative tests of amines ;*

— *the principal uses of nitrogen containing compounds.*

In this unit, we shall focus our attention on the chemistry of organic compounds with functional groups containing nitrogen. The important functional groups containing nitrogen are :

Cyanide	$-C \equiv N$
Isocyanide	$-N \overset{\rightarrow}{=} C$
Nitro	$-N \begin{matrix} \diagup\!\!\!\diagup O \\ \searrow O \end{matrix}$
Nitrite	$-O-N=O$
Primary amino	$-NH_2$
Secondary amino	$>NH$
Tertiary amino	$\begin{matrix} \diagdown \\ -N \\ \diagup \end{matrix}$
Imino	$=NH$
Diazo	$-\overset{+}{N} \equiv N:$ or $-\overset{+}{N}_2$

Let us discuss the chemistry of the above mentioned functional groups.

CYANIDES

Cyanides are characterised by the presence of *cyano* —CN group in their molecules. They are considered to be the derivatives of hydrogen cyanide (HCN) in which H atom is replaced by *alkyl* or *aryl*

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group. If —CN group is linked to alkyl group, the compound is called *alkyl cyanide*, whereas if cyano group is linked directly to aryl group, the compound may be termed as *aryl cyanide*.

R—CN	Ar—CN
Alkyl cyanide	Aryl cyanide

9.1. NOMENCLATURE

In **common system,** cyanides are named by any of the following methods :

(*i*) By using suffix ***cyanide*** after the name of alkyl or aryl group.

Or

(*ii*) By adding the suffix ***onitrile*** in place of ***ic-acid*** in the common name of the corresponding acid produced by the hydrolysis of the cyanide compound.

For example,

CH_3CN on hydrolysis gives CH_3COOH *i.e.*, acetic acid. Therefore, the common name of compound **CH_3CN** is :

Methyl cyanide or *Acetonitrile* as derived below from acetic acid

$$\textit{Acetic acid} \xrightarrow[\text{+ onitrile}]{\text{– ic acid}} \textit{Acetonitrile}$$

In **IUPAC system,** cyanides are named as *Alkanenitriles*. The carbon atom of the —CN group is also counted in the parent chain. The positions of various substituents are indicated by numbering the carbon atoms of the parent chain starting from carbon atom of —CN group. The common and IUPAC names of some cyanide compounds are given below in tabular form.

Molecular formula	*Common name*	*IUPAC name*
$CH_3—CN$	Methyl cyanide or Acetonitrile	Ethanenitrile
$C_2H_5—CN$	Ethyl cyanide or Propiononitrile	Propanenitrile
$^3CH_2 = {}^2CH—{}^1CN$	Vinyl cyanide or Acrylonitrile	2-Propenenitrile
$C_6H_5—CN$	Phenyl cyanide or Benzonitrile	Benzenenitrile
$^3CH_3—{}^2CH(CH_3)—{}^1CN$	Isopropyl cyanide or Isobutyronitrile	2-Methylpropanenitrile

The IUPAC names of some substituted cyanides are given below :

$$\overset{5}{CH_3}\overset{4}{C}H(Cl)\overset{3}{C}H_2\overset{2}{C}H_2\overset{1}{C}N$$

4-Chloropentanenitrile

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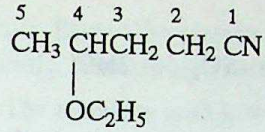
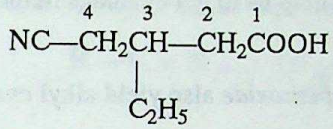
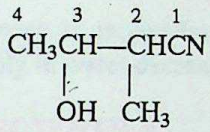
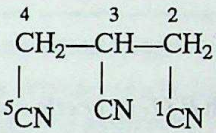

4-Ethoxypentanenitrile


3-Ethyl-4-cyanobutanoic acid


2-Methyl-3-hydroxybutanenitrile


3-Cyano-1, 5-pentanedinitrile

9.2. METHODS OF PREPARATION

Some of the methods of preparation of **cyanides** are :

1. From alkyl halides. Alkyl halides on treatment with *ethanolic solution of sodium cyanide* or *potassium cyanide* give alkyl cyanides.

$$\underset{\text{Alkyl halide}}{RX} + KCN\,(alc.) \longrightarrow \underset{\text{Alkyl cyanide}}{RCN} + KX$$

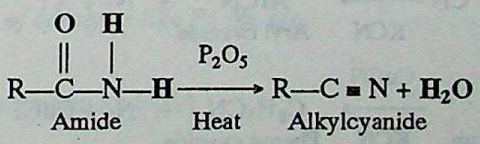
For example,

$$\underset{\text{Bromoethane}}{C_2H_5Br} + KCN\,(alc.) \xrightarrow{\text{Heat}} \underset{\text{Propanenitrile}}{C_2H_5CN} + KBr$$

A small amount of *ethyl isocyanide* (C_2H_5NC) is also formed during the reaction. The method gives satisfactory results for primary and secondary halides. However, with tertiary halides, a considerable amount of *alkene* is also formed due to β-elimination of halides.

This method is not suitable for preparing aryl cyanides because aryl halides are less reactive towards nucleophilic substitution reactions.

2. By dehydration of primary amides. The dehydration of primary amides can be achieved by *phosphorus pentoxide* (P_2O_5) or *thionyl chloride* ($SOCl_2$).



$$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Ethanenitrile}}{CH_3CN} + H_2O$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Benzenenitrile}}{C_6H_5CN} + H_2O$$

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$$\underset{\text{Ethanamide}}{CH_3CONH_2} \xrightarrow{SOCl_2} \underset{\text{Ethanenitrile}}{CH_3CN} + SO_2 + 2HCl$$

This method has an *advantage* in the sense that it can help us to get cyanides in the *pure form.*

3. By dehydration of ammonium carboxylates

Ammonium carboxylate on heating with *phosphorus pentoxide* also yield alkyl cyanides

$$RCOO^{-}NH_4^{+} \xrightarrow[\text{Heat}]{P_2O_5} RCN + 2H_2O$$

$$\underset{\text{Ammonium acetate}}{CH_3COO^{-}NH_4^{+}} \xrightarrow[\text{Heat}]{P_2O_5} \underset{\text{Ethanenitrile}}{CH_3CN} + 2H_2O$$

4. By dehydration of aldoximes. Dehydration of aldoximes with P_2O_5 or *acetic anhydride* also gives cyanides. For example.

$$\underset{\text{Acetaldoxime}}{CH_3CH = NOH} \xrightarrow[-H_2O]{(CH_3CO)_2O} \underset{\text{Ethanenitrile}}{CH_3C \equiv N}$$

$$\underset{\text{Benzaldoxime}}{C_6H_5CH = NOH} \xrightarrow[-H_2O]{(CH_3CO)_2O} \underset{\text{Benzenenitrile}}{C_6H_5CN}$$

5. From Grignard's reagent. This method is particularly useful for preparing tertiary alkyl cyanides. It involves the treatment of the Grignard's reagent with *cyanogen chloride (Cl—CN).*

$$RMgX + Cl—CN \xrightarrow{\text{Ether}} RCN + Mg(X)Cl$$

$$CH_3MgI + Cl—CN \xrightarrow{\text{Ether}} \underset{\text{Methyl cyanide}}{CH_3CN} + Mg(I)Cl$$

6. From aryl diazonium salt. This is a convenient method of preparation of *aryl cyanides* only. It is not suitable for preparing alkyl cyanides because alkyl diazonium salts are quite unstable even at low temperatures. It involves the treatment of *benzene diazonium salt with a mixture of copper(I) cyanide and sodium or potassium cyanide.*

$$\underset{\text{Aryl diazonium salt}}{Ar\overset{+}{N_2}\overset{-}{X}} + :\overset{-}{C}N \xrightarrow[\text{KCN}]{\text{CuCN}} \underset{\text{Aryl cyanide}}{ArCN} + N_2 + \overset{-}{X}:$$

$$\underset{\text{Benzenediazonium chloride}}{C_6H_5\overset{+}{N_2}\overset{-}{Cl}} \xrightarrow[\text{KCN}]{\text{CuCN}} \underset{\text{Phenyl cyanide}}{C_6H_5CN} + N_2 + CuCl$$

This reaction is a special case of ***Sandmeyer's reaction.***

9.3. PHYSICAL PROPERTIES

1. Physical state and smell. The lower members of the family are colourless liquids whereas the higher members are crystalline solids. They are stable compounds with *pleasant smell.*

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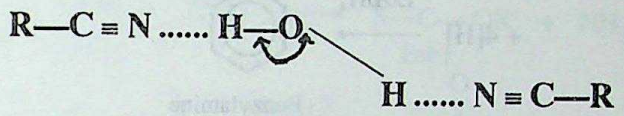
2. Boiling points. Due to the presence of polar —C ≡ N group in the molecules, they have high dipole moment and consequently, possess high melting and boiling points.

3. Solubility. The cyanides with low molecular mass are soluble in water. *This is due to the tendency of their molecules to form hydrogen bonds with water molecules.*



With the increase in molecular mass, the bulk of the non-polar portion (*i.e.*, R—) increases and consequently, solubility in water decreases. However, the cyanides are fairly soluble in organic solvents.

9.4. CHEMICAL PROPERTIES

Some of the important chemical properties of alkanenitriles are described as follows :

1. Hydrolysis. *Nitriles* can be hydrolysed in acidic as well as in basic conditions to give amides as the initial products. Exhaustive hydrolysis results in the formation of carboxylic acid and ammonia.

Acidic hydrolysis. Acidic hydrolysis produces carboxylic acid and ammonium salt.

$$\underset{\text{Nitrile}}{RCN} \xrightarrow[HOH]{H_3O^+} \underset{\text{Amide}}{RCONH_2} \xrightarrow[HOH]{HCl} \underset{\text{Acid}}{RCOOH} + \underset{\text{Ammonium salt}}{NH_4^+}$$

$$\underset{\text{Ethanenitrile}}{CH_3CN} \xrightarrow[HOH]{H_3O^+} CH_3CONH_2 \xrightarrow[HOH]{HCl} \underset{\text{Ethanoic acid}}{CH_3COOH} + NH_4Cl$$

Basic hydrolysis. Basic hydrolysis produces salt of the carboxylic acid and ammonia.

$$\underset{\text{Nitrile}}{RCN} \xrightarrow[HOH]{OH^-} \underset{\text{Amide}}{RCONH_2} \xrightarrow[HOH]{OH^-} \underset{\text{Salt of acid}}{RCOO^-} + NH_3$$

$$CH_3CN \xrightarrow[HOH]{OH^-} CH_3CONH_2 \xrightarrow[HOH]{NaOH} CH_3COONa + NH_3$$

Hydrolysis of nitriles can be stopped selectively at the amide stage.

2. Reduction

(*a*) ***Complete reduction or strong reduction.*** Nitriles undergo reduction to form *primary amines* as the products. This type of reduction can be carried out by any of the following :

(*i*) *H_2 in the presence of catalysts like Pt, Ni, etc.*

(*ii*) *Na/C_2H_5OH*

(*iii*) *$LiAlH_4$ (lithium aluminium hydride)*

For example,

$$\underset{\text{Cyanide}}{RC \equiv N} + 2H_2 \xrightarrow{\text{Pt or Ni}} \underset{\text{Primary amine}}{RCH_2NH_2}$$

$$R—C \equiv N + 4[H] \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} \underset{\text{Amine}}{RCH_2NH_2}$$

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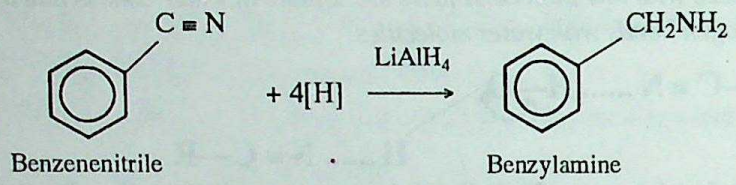
$$\underset{\text{Propanenitrile}}{CH_3CH_2CN} \xrightarrow{LiAlH_4} \underset{\text{Propanamine}}{CH_3CH_2CH_2NH_2}$$



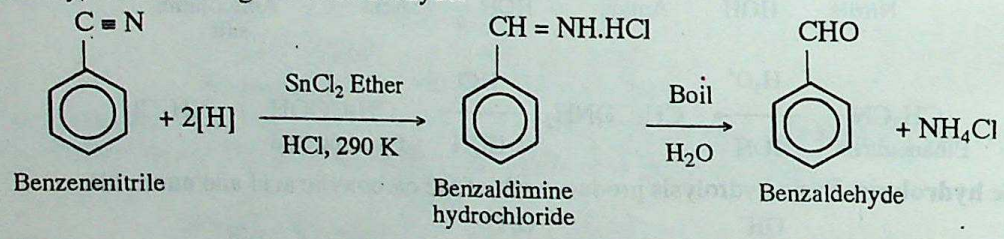
Chemical reduction of alkyl or aryl cyanides using $LiAlH_4$ or *Na/ethanol* is referred to as **Mendius reaction.**

(*b*) **Partial reduction or mild reduction.** When reduction is carried out with acidified stannous chloride ($SnCl_2/HCl$) at room temperature, imine hydrochloride is obtained which on subsequent hydrolysis with boiling water gives *aldehyde*. This specific type of reduction of cyanides is called **Stephen's reduction.**

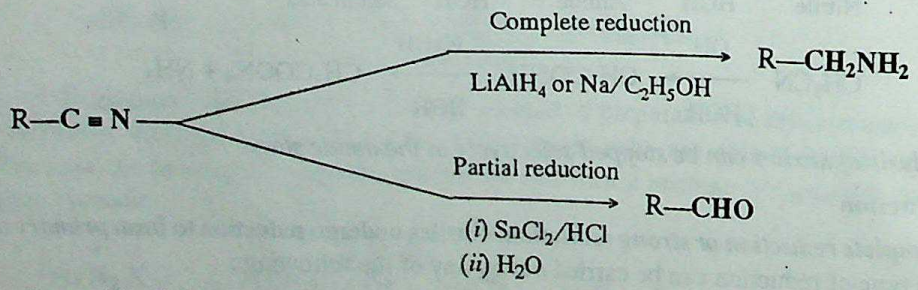
$$SnCl_2 + 2HCl \longrightarrow SnCl_4 + 2[H]$$

$$\underset{\text{Ethanenitrile}}{CH_3C \equiv N} + 2[H] + HCl \xrightarrow[290\ K]{Ether} \underset{\text{Acetaldimine hydrochloride}}{CH_3CH = NH.HCl} \xrightarrow{H_2O,\ Boil} \underset{\text{Acetaldehyde}}{CH_3CHO} + NH_4Cl$$

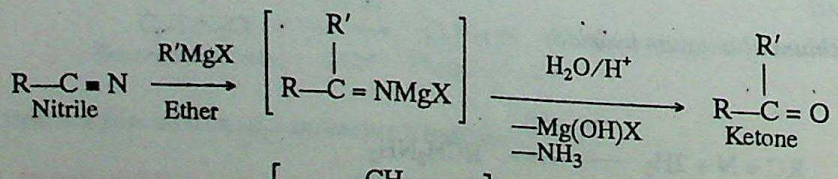
Similarly, benzonitrile gives benzaldehyde.

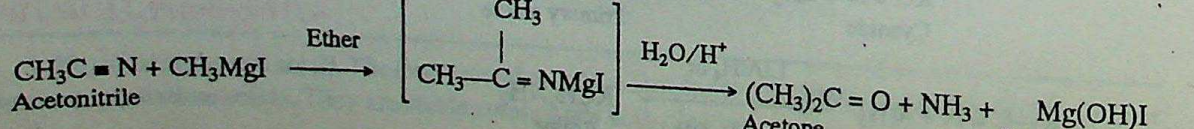


In short,



3. Reaction with Grignard's reagent. Grignard reagents add on to nitriles forming imine salt intermediate which on subsequent hydrolysis gives ketone.





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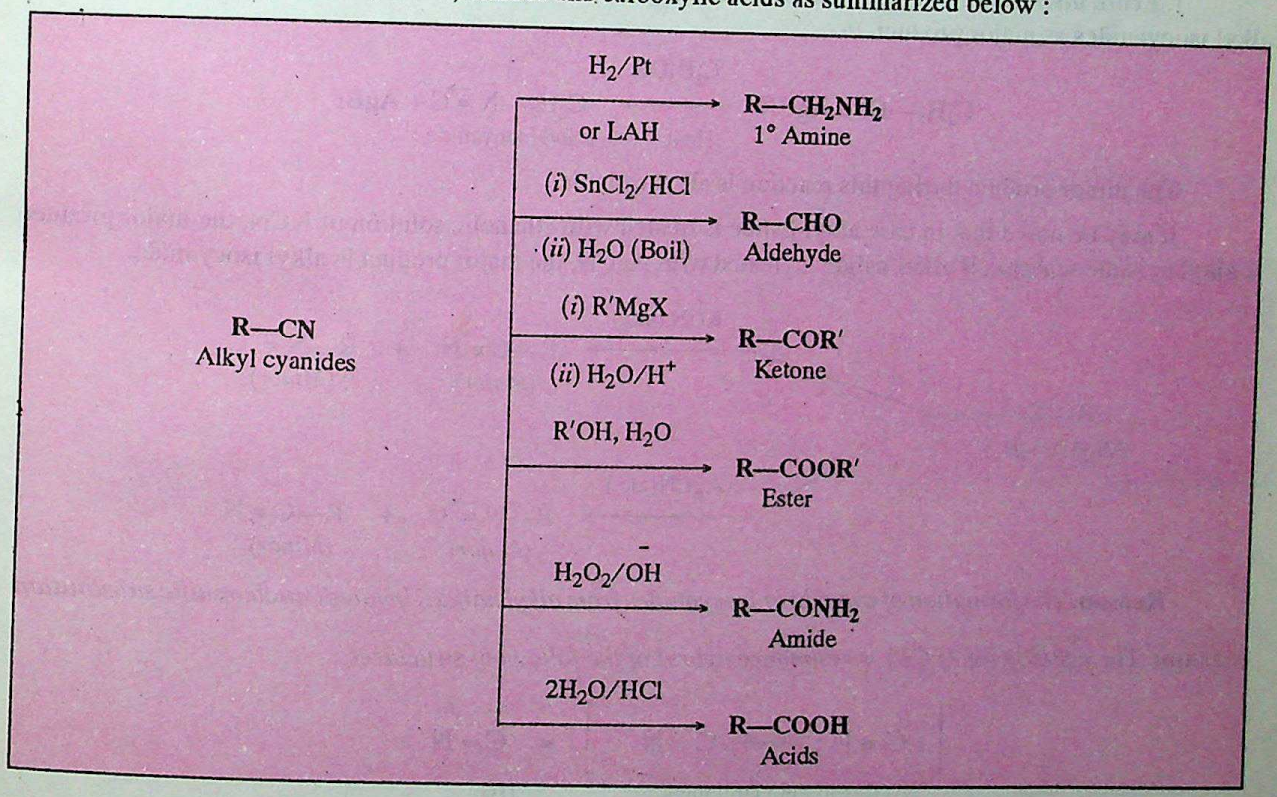
4. Alcoholysis. When alcoholic solution of alkylcyanides is heated with concentrated sulphuric acid or hydrochloric acid, an *ester* is produced.

$$\underset{\text{Alkyl cyanide}}{RC\equiv N} + \underset{\text{Alcohol}}{R'OH} + H_2O \xrightarrow{H^+} \underset{\text{Ester}}{R-\overset{\overset{O}{\|}}{C}-OR'} + NH_4^+$$

$$\underset{\text{Ethane nitrile}}{2CH_3C\equiv N} + 2C_2H_5OH + 2H_2O \xrightarrow[\text{Heat}]{H_2SO_4} \underset{\text{Ethyl ethanoate}}{2CH_3-\overset{\overset{O}{\|}}{C}-OC_2H_5} + (NH_4)_2SO_4$$

Uses.

1. Ethanenitrile is used as a solvent particularly in perfume industry.
2. Nitriles are also used in the manufacture of *nitrile rubber* and also in textile industry.
3. The nitriles are useful intermediates in organic synthesis because, they can be converted into *p*-amines, aldehydes, ketones, esters, amides and carboxylic acids as summarized below :



ISOCYANIDES or CARBYLAMINES

Isocyanides are structural isomers of alkyl cyanides. In these compounds, the —C ≡ N group is linked to the alkyl or aryl group through N atom. Thus, they have general formula

$$\underset{\text{Alkyl isocyanide}}{R-N\overset{\rightarrow}{=}C} \quad \text{or} \quad \underset{\text{Aryl isocyanide}}{Ar-N\overset{\rightarrow}{=}C}$$

9.5. NOMENCLATURE

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In **common system**, these are generally named as *alkyl isocyanides*. They can also be named by adding a prefix *iso* before the name of the isomeric *alkyl nitriles*.

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In **IUPAC system,** isocyanides are named as *alkyl carbylamine*. The names of some isocyanides are given as follows :

Formula	*Common name*	*IUPAC name*
CH_3NC	Methyl isocyanide or Acetoisonitrile	Methyl carbylamine
CH_3CH_2NC	Ethyl isocyanide or Propionoisonitrile	Ethyl carbylamine
$CH_3CH_2CH_2NC$	Propyl isocyanide or Butyroisonitrile	Propyl carbylamine

9.6. METHODS OF PREPARATION

Some of the methods of preparation of isocyanides are :

1. **From alkyl halides.** Alkyl halides, on heating with ethanolic solution of AgCN (silver cyanide) give alkyl isocyanides as major product.

$$C_2H_5\text{—}Br + AgCN \xrightarrow[\text{Heat}]{C_2H_5OH} \underset{\text{Ethyl isocyanide}}{C_2H_5\text{—}N \overset{\rightarrow}{=} C} + AgBr$$

The minor product during this reaction is alkyl cyanide.

It may be noted that in case alkyl halide is treated with ethanolic solution of KCN, the major product is alkyl cyanide whereas if alkyl halide is treated with AgCN, the major product is alkyl isocyanide.

$$\underset{\text{Alkyl halide}}{R\text{—}X} \xrightarrow{KCN\ (alc.)} \underset{(Major)}{R\text{—}C \equiv N} + \underset{(Minor)}{R\text{—}N \overset{\rightarrow}{=} C}$$

$$\underset{\text{Alkyl halide}}{R\text{—}X} \xrightarrow{AgCN\ (alc.)} \underset{(Major)}{R\text{—}N \overset{\rightarrow}{=} C} + \underset{(Minor)}{R\text{—}C \equiv N}$$

Reason. *The formation of cyanide or isocyanides from alkyl halides involves* ***nucleophilic substitution reaction.*** *The cyanide ion* ($:\bar{C}N$) *is resonance hybrid of the following structures :*

$$\underset{\text{Resonating structures}}{\left[:\bar{C} \equiv N : \longleftrightarrow : C = \ddot{N}^{-} : \right]} \equiv \underset{\text{Hybrid structure}}{\overset{\delta-}{C} \cdots \overset{\delta-}{N}}$$

As is evident from the hybrid structure, cyanide is capable of attacking the molecule through C atom as well as through N atom. Such a nucleophilic species which is capable of attacking the molecule through two sites is called ambident nucleophile. Thus, $\bar{C}N$ *is an ambident nucleophile.*

Now, KCN is predominantly ionic. Therefore, both carbon and nitrogen atoms are free to donate electron pair. Since carbon-carbon bond is relatively stronger than carbon-nitrogen bond, therefore, in this case attack mostly occurs through the carbon atom of the cyanide group and ***alkyl cyanides*** *are the major products.*

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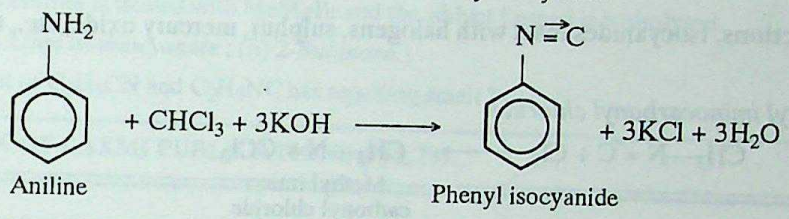
Silver cyanide Ag—CN on the other hand, is predominantly ***covalent.*** *Thus, in this case only N atom is free to act as donor of electron pair, and the attack mostly occurs through the N atom of cyanide group giving* ***alkyl isocyanides*** *as the major product.*

2. From Amines. When primary amines are heated with chloroform in the presence of KOH, isocyanides are formed. This reaction is known as **carbylamine reaction.**

$$\underset{\text{Ethyamine}}{C_2H_5NH_2} + CHCl_3 + 3KOH \longrightarrow \underset{\text{Ethyl isocyanide}}{C_2H_5NC} + 3KCl + 3H_2O$$



9.7. PHYSICAL PROPERTIES

1. Physical state

Isocyanides are colourless liquids with intolerable smell.

2. Boiling points

They are relatively less polar in comparison with isomeric cyanides. Consequently, their melting and boiling points are relatively low in comparison with the cyanides of same molecular mass.

Compound	*Mol. mass*	*B.P. (K)*
$CH_3—C \equiv N$ Methyl cyanide	41	355
$CH_3—N \equiv C$ Methyl isocyanide	41	322

3. Solubility

They are partially soluble in water.

9.8. CHEMICAL PROPERTIES

1. Hydrolysis. They undergo hydrolysis in acidic medium to form formic acid and primary amines.

$$R—N \equiv C + 2HOH \xrightarrow{H^+} \underset{p\text{-amine}}{RNH_2} + HCOOH$$

$$\underset{\text{Ethyl isocyanide}}{C_2H_5—N \equiv C} + 2HOH \xrightarrow{H^+} \underset{\text{Ethyl amine}}{C_2H_5NH_2} + HCOOH$$

They ***do not hydrolyse in alkaline medium.***

The basic hydrolysis is initiated by the attack of $\overset{-}{O}H$ ion on the substrate molecule, but in alkyl isocyanide ($R—\overset{+}{N} \equiv \overset{-}{C}$:), the carbon atom of isocyanide group being negatively charged, resists the attack of $\overset{-}{O}H$ ions. However, it readily undergoes the attack of H^+ in acidic medium.

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2. Reduction. Isocyanides on reduction with H_2/Ni or H_2/Pt or Na/alcohol give ***secondary amines.*** The —NC group gets reduced to **—NH(CH_3)** group.

$$\underset{\text{Alkyl isocyanide}}{R—N\overset{\rightarrow}{=}C} + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{N-Methyl alkanamine}}{R—NH—CH_3}$$

$$C_2H_5—N\overset{\rightarrow}{=}C + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{N-Methyl ethanamine}}{C_2H_5—NH—CH_3}$$

3. Addition reactions. Isocyanides react with halogens, sulphur, mercury oxide, etc., to form addition products. For example,

(*a*) *Cl_2 gives alkyl iminocarbonyl chloride*

$$CH_3—N\overset{\rightarrow}{=}C + Cl_2 \longrightarrow \underset{\text{Methyl imino carbonyl chloride}}{CH_3—N = CCl_2}$$

(*b*) *Sulphur gives alkyl isothiocyanate*

$$CH_3—N\overset{\rightarrow}{=}C + \tfrac{1}{8}S_8 \longrightarrow \underset{\text{Methyl isothiocyanate}}{CH_3—N = C = S}$$

(*c*) *Mercuric oxide gives alkyl isocyanate*

$$CH_3—N\overset{\rightarrow}{=}C + 2HgO \longrightarrow \underset{\text{Methyl isocyanate}}{CH_3—N = C = O} + Hg_2O$$

The famous Bhopal tragedy in December 1984 was caused by methyl isocyanate (MIC).

4. Isomerisation. Alkyl isocyanides on heating are converted into relatively more stable alkyl cyanides.

$$\underset{\text{Alkyl isocyanide}}{R—N\overset{\rightarrow}{=}C} \xrightarrow{Heat} \underset{\text{Alkyl cyanide}}{R—C \equiv N}$$

Distinction between ethyl cyanide and ethyl isocyanide

Ethyl cyanide	*Ethyl isocyanide*
1. Hydrolysis $C_2H_5CN \xrightarrow{H_2O/H^+} C_2H_5COOH + NH_4^+$ Propanoic acid	$C_2H_5NC \xrightarrow{H_2O/H^+} C_2H_5NH_2 + HCOOH$ Ethylamine
2. Reduction $C_2H_5CN \xrightarrow[HCl]{Zn-Hg} C_2H_5CH_2NH_2$ *n*-Propyl amine	$C_2H_5NC \xrightarrow[HCl]{Zn-Hg} C_2H_5NCH_3$ Ethylmethyl amine
3. Boiling point *b.p.* = 344 K	*b.p.* = 352 K
4. Solubility in water Appreciably soluble	Sparingly soluble

REVIEW PROBLEMS

9.1. Give the structure of vinyl cyanide and write its IUPAC name. **Ans.** *$CH_2 = CHCN$; Prop-2-enenitrile*

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9.2. Which of the following are ambident nucleophiles ?

$$\bar{R}O:,\ :\bar{C}N,\ :\bar{C}NS,\ H_2\ddot{O}:\ :\bar{N}O_2$$

Ans. $\bar{C}N$, $\bar{C}NS$, $\bar{N}O_2$

9.3. Suggest a method to convert ethanenitrile to 2-butanone. **Ans.** (*i*) C_2H_5MgBr, (*ii*) H_2O/H^+

9.4. Which products are formed in each of the following cases. Give equations.

(*i*) Ethyl isocyanide is allowed to react with S_8.

(*ii*) Ethanenitrile is treated with MeMgBr and the adduct formed is hydrolysed.

[**Hint.** (*i*) *Ethyl isothiocyanate* ; (*ii*) *2-Butanone.*]

9.5. Which out of C_2H_5CN and C_2H_5NC has repelling smell ? **Ans.** C_2H_5NC

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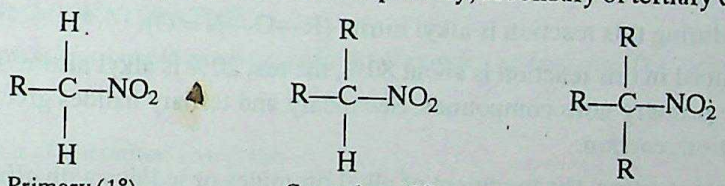
NITRO COMPOUNDS

Nitro compounds are characterised by the presence of *nitro group* (—NO_2) in their molecules. They may be aliphatic or aromatic compounds according as the nitro group is attached to *alkyl* or *aryl group.*

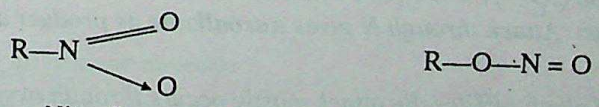
R—NO_2	Ar—NO_2
Aliphatic nitro compound	Aromatic nitro compound

The aliphatic nitro compounds may be further classified into primary, secondary or tertiary nitro compounds according as the nitro group is attached to primary, secondary or tertiary carbon atom respectively.



Primary (1°) Secondary (2°) Tertiary (3°)

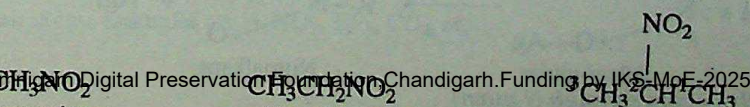
It may be noted that NO_2 group is also an **ambident group** and is capable of getting attached to carbon chain through nitrogen $\left[-N\begin{matrix}\nearrow O\\ \searrow O\end{matrix}\right]$ as well as through oxygen (—O—N = O) atom. The compounds in which NO_2 is linked to the alkyl or aryl group through oxygen atom are called **nitrites.** Nitrites are isomeric with nitro compounds.



Nitroalkanes Alkyl nitrites

9.9. NOMENCLATURE

Nitro compounds are named by using the prefix *nitro* before the name of parent hydrocarbon. Thus, aliphatic nitro compounds are called **nitroalkanes** while aromatic nitro compounds are called **nitroarenes.** The position of nitro group and other substituents if any are indicated by the arabic numerals. Some examples are :



Nitromethane Nitroethane 2-Nitropropane

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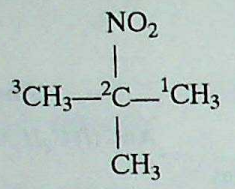
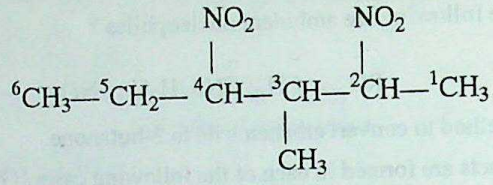
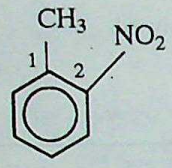


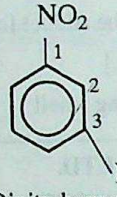
2-Methyl-2-nitropropane



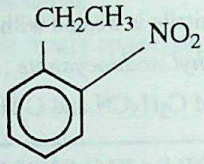
3-Methyl-2, 4-dinitrohexane



2-Nitrotoluene



1, 3-Dinitrobenzene



2-Nitroethylbenzene

9.10. METHODS OF PREPARATION

1. From alkyl halides. Alkyl halides (especially bromides or iodides) when treated with *silver nitrite* in ethanolic solution give nitro compounds.

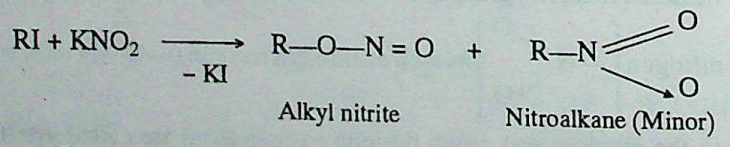
$$R—I + AgNO_2 \longrightarrow \underset{\text{Nitroalkane}}{R—NO_2} + AgI$$

$$C_2H_5I + AgNO_2 \longrightarrow \underset{\text{Nitroethane}}{C_2H_5—NO_2} + AgI$$

A minor product during this reaction is alkyl nitrite (R—O—N = O).

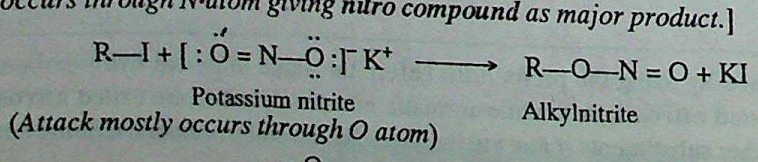
Nitroalkane produced in this reaction is about 80%, the rest 20% is alkyl nitrite. The above method is primarily used to prepare primary nitro compounds. Secondary and tertiary halides give major proportion of alkenes due to β-elimination reaction.

In contrast to above reaction, the treatment of alkyl bromides or iodides with *alkali nitrites* give *alkyl nitrites* as major product along with nitroalkanes as minor product.

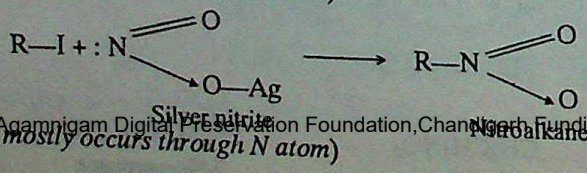


Explanation. *Nitrite ion* (:$\ddot{\underset{..}{O}}$—$\ddot{N}$ = $\ddot{O}$:), *like cyanide ion is also an ambident nucleophile (having two attacking sites, N and O atoms). Attack through N gives* ***nitroalkane*** *as product and attack through oxygen gives* ***alkyl nitrite*** *as product.*

Due to ionic nature of alkali nitrites the attack mostly occurs through oxygen because C—O bond is relatively stronger. However, in case of silver nitrite, which has considerable ***covalent*** *character, the attack mostly occurs through N-atom giving* ***nitro compound*** *as major product.*]



(*Attack mostly occurs through O atom*)



(*Attack mostly occurs through N atom*)

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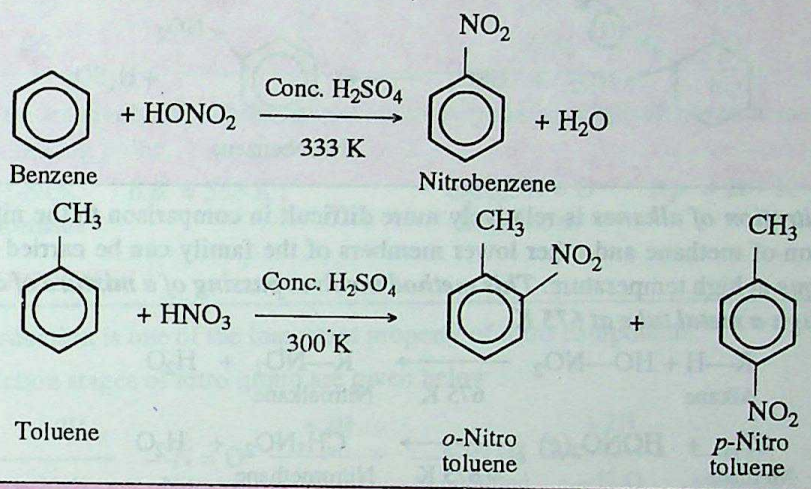
It may be noted that even $NaNO_2$ or KNO_2 gives a fairly good yield (about 60%) of nitro compound if the reaction is carried out in solvents like dimethyl formamide (DMF) or dimethyl sulphoxide (DMSO).

Above method is not applicable for the preparation of aromatic nitro compounds because of the less reactivity of aryl halides towards nucleophilic substitution.

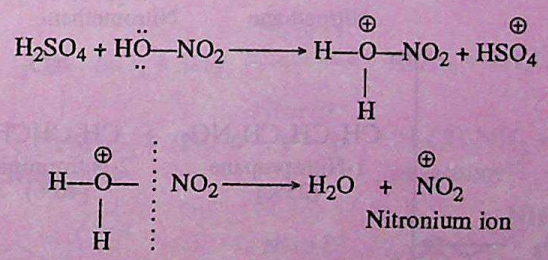
2. By direct nitration. This method is quite suitable to get ***aromatic nitro compounds***. For example, nitrobenzene is produced when benzene is allowed to react with a mixture of concentrated nitric acid and concentrated sulphuric acid (also called *nitrating mixture*).



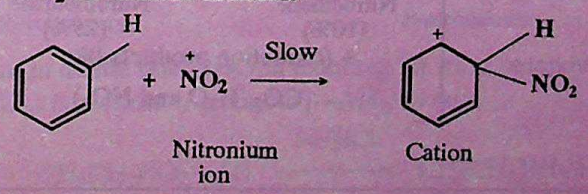
MECHANISM OF NITRATION

This reaction is an example of ***electrophilic* substitution of benzene.*** The various steps through which the reaction proceeds are :

(*i*) Generation of nitronium ($\overset{+}{N}O_2$) ion



(*ii*) Attack of $\overset{\oplus}{N}O_2$ on benzene molecule



*An electrophile is an electron deficient species which attacks the electron rich centre. It should be able to act as acceptor of electron pair. Some examples are $\overset{\oplus}{H}$, $\overset{\oplus}{N}O_2$, BF_3, CO_2, etc.

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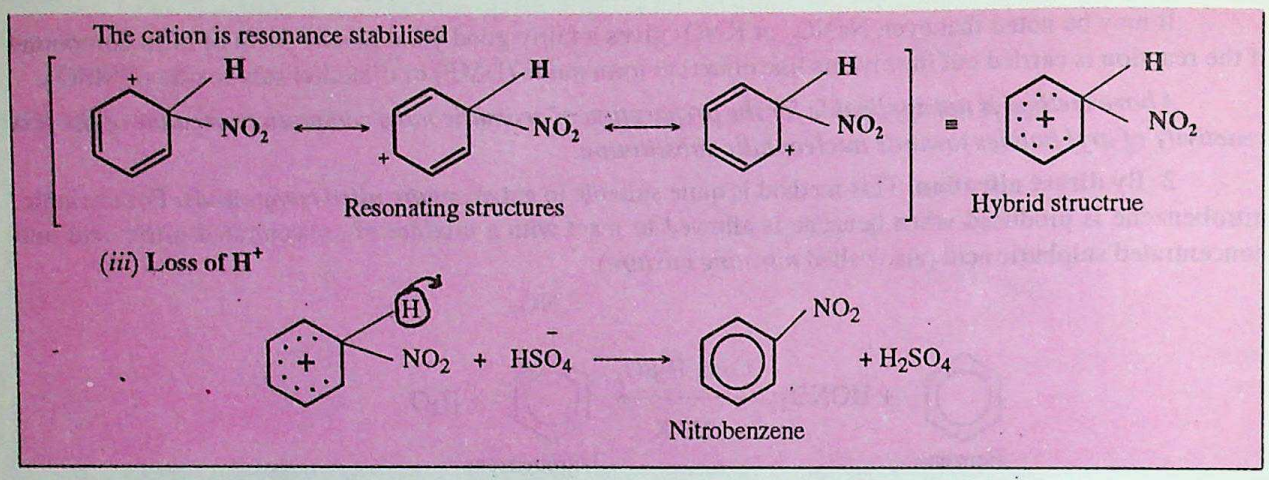

Direct nitration of alkanes is relatively more difficult in comparison to the nitration of arenes. For example, nitration of methane and other lower members of the family can be carried out by *vapour phase nitration technique* at high temperature. ***This method involves passing of a mixture of alkane and vapour of nitric acid through a metal tube at 675 K.***

$$\underset{\text{Alkane}}{R{-}H} + HO{-}NO_2 \xrightarrow[675\ K]{} \underset{\text{Nitroalkane}}{R{-}NO_2} + H_2O$$

$$\underset{\text{Methane}}{CH_4} + HONO_2(g) \xrightarrow[\approx 675\ K]{} \underset{\text{Nitromethane}}{CH_3NO_2} + H_2O$$

Limitation. Since the process occurs at high temperature therefore, C—C bond of alkanes also undergoes cleavage at this temperature and a mixture of nitroalkanes are formed. For example, the products of nitration of ethane and propane are being given is follows :

$$\underset{\text{Ethane}}{CH_3CH_3} + HNO_3 \xrightarrow{675\ K} \underset{\text{Nitroethane}}{CH_3CH_2NO_2} + \underset{\text{Nitromethane}}{CH_3NO_2}$$

$$\underset{\text{Propane}}{CH_3CH_2CH_3} + HNO_3 \longrightarrow \left[\begin{array}{l} \underset{\substack{\text{1-Nitropropane}\\(25\%)}}{CH_3CH_2CH_2NO_2} + \underset{\substack{\text{2-Nitropropane}\\(40\%)}}{CH_3\overset{\overset{NO_2}{|}}{C}HCH_3} \\ \underset{\substack{\text{Nitroethane}\\(10\%)}}{CH_3CH_2NO_2} + \underset{\substack{\text{Nitromethane}\\(25\%)}}{CH_3{-}NO_2} \\ \text{+ (oxidation products like } CO_2, H_2O \text{ and } NO_2) \end{array}\right]$$

9.11. PHYSICAL PROPERTIES

1. Physical state. Lower nitroalkanes are colourless liquids with pleasant smell. Aromatic nitro compounds like nitrobenzene have pale yellow colour. Nitrobenzene, particularly has a smell of bitter almonds.

2. Solubility. Nitroalkanes are sparingly soluble in water (lower members are relatively more soluble than the higher members). Aromatic nitro compounds are not soluble in water at all. They are soluble in organic solvents.

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3. Boiling points.

(*a*) The nitro compounds are highly polar with the dipole moments ranging approximately between 3 to 4D. Thus, they have strong dipole-dipole interactions which cause them to have high boiling points in comparison to the hydrocarbons of comparable molecular masses.

Compound	*b.p.(K)*	*Hydrocarbon*	*b.p.(K)*
CH_3NO_2 (61)	374	C_4H_{10} (58)	138
$C_2H_5NO_2$ (75)	388	C_5H_{12} (72)	144
$C_6H_5NO_2$ (123)	483	C_6H_6 (78)	353

(*b*) Nitroalkanes are relatively more polar than their corresponding alkyl nitrite isomers and therefore, they have relatively high boiling points

$C_2H_5NO_2$ (Nitroethane) *b.p.* = *388 K*; $C_2H_5ON = O$ (Ethylnitrite) *b.p.* = 261 K

9.12. CHEMICAL PROPERTIES

1. Reduction. Reduction is one of the important property of nitro compounds.

The various reduction stages of nitro group are given below :

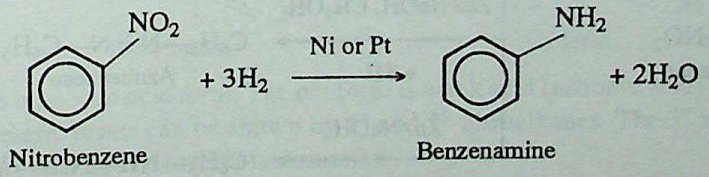
$$\underset{\text{Nitro}}{-NO_2} \xrightarrow[-H_2O]{+2H} \underset{\text{Nitroso}}{-N=O} \xrightarrow{+2H} \underset{\text{Substituted hydroxylamine}}{-NHOH} \xrightarrow[-H_2O]{+2H} \underset{p\text{-Amine}}{-NH_2}$$

The final product, however, depends upon the nature of reducing agent as well as the pH of the medium as described below :

(*i*) **Catalytic reduction.** Both aliphatic and aromatic nitro compounds are reduced to 1°-*amines*, on reaction with H_2/Ni or H_2/Pt or H_2/Pd.

$$R-NO_2 + 3H_2 \xrightarrow{\text{Ni or Pt}} RNH_2 + 2H_2O$$

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + 3H_2 \xrightarrow{\text{Ni or Pt}} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + 2H_2O$$



(*ii*) **Reduction in acidic medium.** On reducing the nitro compounds with *Zn/HCl, Fe/HCl* or *Sn/HCl, the nitro group (—NO₂)* is reduced to *p-amino (—NH₂) group.*

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} + 6H \xrightarrow{Fe/HCl} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + 2H_2O$$

$$\underset{\text{Nitrobenzene}}{C_6H_5NO_2} + 6H \xrightarrow{Sn/HCl} \underset{\text{Aniline}}{C_6H_5NH_2} + 2H_2O$$

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(*iii*) **Reduction in neutral medium.** When reduction is carried out using *Zn/NH₄Cl(aq)*, the *nitro group* (*—NO₂*) is reduced to *—NHOH* group giving substituted hydroxyl amines as the products.

$$\underset{\text{Nitromethane}}{CH_3—NO_2} + 4[H] \xrightarrow{Zn/NH_4Cl} \underset{\text{N-Methylhydroxyl amine}}{CH_3—NHOH} + H_2O$$

$$\underset{\text{Nitrobenzene}}{C_6H_5—NO_2} + 4[H] \xrightarrow{Zn/NH_4Cl} \underset{\text{N-Phenyl hydroxyl amine}}{C_6H_5—NHOH} + H_2O$$

The hydroxyl amines on warming with ammonical silver nitrate solution (**Tollen's reagent**) get oxidised to nitroso compound and reduce the Tollen's reagent to metallic silver. This reaction is used as a test for nitro compounds and is also known as ***Baker-Mulliken's test.***

(*iv*) **Reduction with $LiAlH_4$ (Lithium aluminium hydride)**

Alphatic nitro compounds are reduced to *p-amines* with $LiAlH_4$.

$$\underset{\text{Nitromethane}}{CH_3NO_2} \xrightarrow[\text{Ether}]{LiAlH_4} \underset{\text{Methyl amine}}{CH_3NH_2}$$

Aromatic nitro compounds on reduction with $LiAlH_4$ give azo compounds

$$\underset{\text{Nitrobenzene}}{2C_6H_5NO_2} \xrightarrow{LiAlH_4} \underset{\text{Azobenzene}}{C_6H_5—N = N—C_6H_5} + 2H_2O$$

(*v*) **Reduction in alkaline medium.** Aromatic nitro compounds undergo ***biomolecular reduction*** in alkaline medium. Different products are formed with different reducing agents. Some reduction products of nitrobenzene are given below :

$$\underset{\text{Nitrobenzene}}{2C_6H_5NO_2} \xrightarrow[+6H]{Na_3AsO_3/NaOH \text{ or glucose/NaOH}} \underset{\text{Azoxybenzene}}{C_6H_5—N = \overset{O}{\overset{\uparrow}{N}}—C_6H_5} + 3H_2O$$

$$\xrightarrow[+8H]{Zn/NaOH,\ CH_3OH} \underset{\text{Azobenzene}}{C_6H_5—N = N—C_6H_5} + 4H_2O$$

$$\xrightarrow[+10H]{Zn/NaOH} \underset{\text{Hydroazobenzene}}{C_6H_5—NH—NH—C_6H_5} + 4H_2O$$

(*vi*) **Electrolytic reduction.** Electrolytic reduction of nitrobenzene in weakly acidic medium gives aniline whereas, if the reduction is carried out in strongly acidic medium, *p*-aminophenol is formed.

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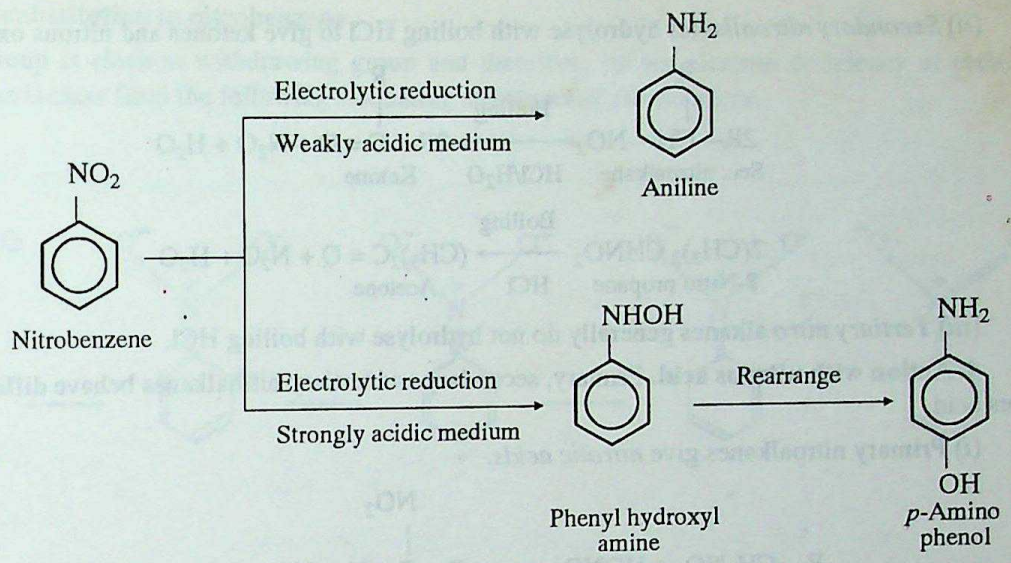
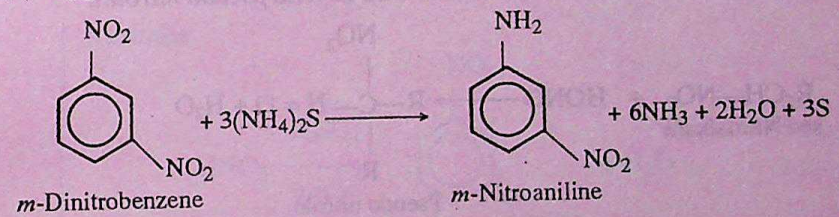
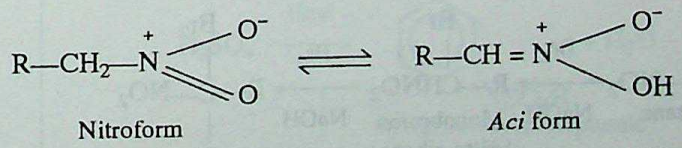


Selective Reduction. If more than one nitro groups are linked to the aromatic ring, then selective reduction of one of the —NO_2 group can be achieved without affecting the other nitro groups by using very mild reducing agent *ammonium sulphide,* $(NH_4)_2S$ or *Sodium polysulphide* (Na_2S_x).



2. Tautomerism in Nitroalkanes. Nitroalkanes are neutral to litmus. But in strong alkaline medium they behave as acids and form salts. Consequently, they are called ***pseudo acids.*** The acidic character is explained on the basis of tautomeric forms which exist in equilibrium



Nitro form is *pseudo acid form.* The *aci* form is weak acid (nitronic acid) and can form salt with strong bases. Such tautomeric forms can be shown by 1° and 2° nitroalkanes. The 3° nitroalkanes do not have α-H atom and therefore, they do not exhibit tautomerism.

3. Hydrolysis. (*i*) *Primary nitroalkanes* can be hydrolysed by boiling with concentrated solution of HCl or approximately 85% H_2SO_4 to give carboxylic acid and hydroxyl amine.

$$\underset{\text{Nitroalkane}}{R—CH_2—NO_2} + H_2O \xrightarrow{HCl} \underset{\text{Carboxylic acid}}{RCOOH} + \underset{\text{Hydroxylamine hydrochloride}}{NH_2OH.HCl}$$

$$\underset{\text{Nitroethane}}{CH_3CH_2—NO_2} + H_2O \xrightarrow{HCl} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Hydroxylamine hydrochloride}}{NH_2OH.HCl}$$

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(*ii*) *Secondary nitroalkanes* hydrolyse with boiling HCl to give ketones and nitrous oxide.

$$\underset{\text{Sec. nitroalkane}}{2R-\overset{\overset{R}{|}}{CH}-NO_2} \xrightarrow[HCl/H_2O]{\text{Boiling}} \underset{\text{Ketone}}{2R-\overset{\overset{R}{|}}{C}=O} + N_2O + H_2O$$

$$\underset{\text{2-Nitro propane}}{2(CH_3)_2CHNO_2} \xrightarrow[HCl]{\text{Boiling}} \underset{\text{Acetone}}{(CH_3)_2C=O} + N_2O + H_2O$$

(*iii*) *Tertiary nitro* alkanes generally do not hydrolyse with boiling HCl.

4. Action with nitrous acid. Primary, secondary and tertiary nitroalkanes behave differently towards nitrous acid.

(*i*) Primary nitroalkanes give *nitrolic acids*.

$$\underset{p\text{-nitroalkane}}{R-CH_2NO_2} + HONO \longrightarrow \underset{\text{Nitrolic acid}}{R-\overset{\overset{NO_2}{|}}{C}=N-OH} + H_2O$$

Nitrolic acid gives red colour with NaOH.

(*ii*) Secondary nitroalkanes react with nitrous acid to form *pseudo nitroles*.

$$\underset{\text{sec-Nitroalkane}}{R_2CH-NO_2} + HONO \longrightarrow \underset{\text{Pseudo nitrole}}{R-\underset{\underset{R}{|}}{\overset{\overset{NO_2}{|}}{C}}-N=O} + H_2O$$

(*iii*) Tertiary nitroalkanes do not react with HNO_2 since they have no α-H atom.

5. Substitution in alkyl group (Halogenation). Primary and secondary nitroalkanes on treatment with Cl_2 or Br_2 in the presence of NaOH give *halonitroalkanes*. The α-H atoms of nitroalkanes are successively replaced by halogen atoms.

$$\underset{p\text{-nitroalkane}}{R-CH_2-NO_2} \xrightarrow[NaOH]{Br_2} \underset{\text{Monobromo nitro alkane}}{R-\overset{\overset{Br}{|}}{C}HNO_2} \xrightarrow[NaOH]{Br_2} \underset{\text{Dibromonitro alkane}}{R-\underset{\underset{Br}{|}}{\overset{\overset{Br_2}{|}}{C}}-NO_2}$$

$$\underset{\text{sec-Nitroalkane}}{R-\underset{\underset{R}{|}}{CH}-NO_2} \xrightarrow[-HBr]{Br_2/NaOH} \underset{\text{α-Bromo derivative}}{R-\underset{\underset{R}{|}}{\overset{\overset{Br}{|}}{C}}-NO_2}$$

Nitromethane reacts with Cl_2 in the presence of NaOH to give chloropicrin.

$$CH_3NO_2 + 3Cl_2 + 3NaOH \longrightarrow \underset{\text{Chloropicrin}}{Cl_3CNO_2} + 3NaCl + 3H_2O$$

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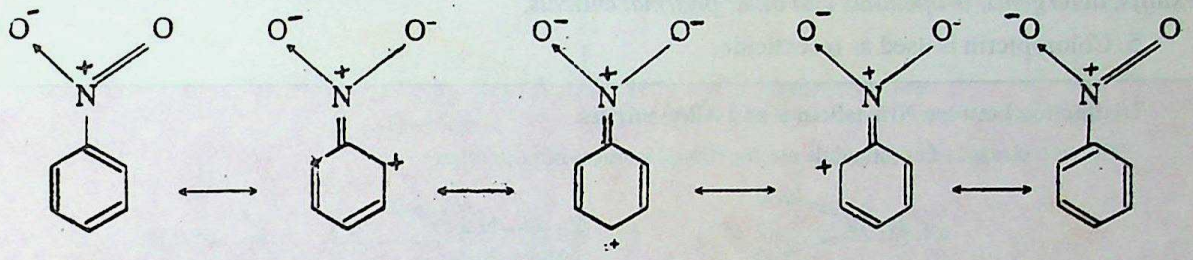
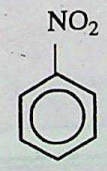
6. Ring substitution in nitrobenzene

Nitro group is electron withdrawing group and therefore, causes electron deficiency at ortho and para-positions as is clear from the following resonating structures of nitrobenzene.



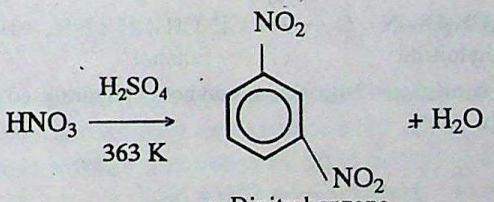
Resonating structures

Thus, it is evident that the *m*-position is relatively rich in electron density and therefore, electrophilic attack is more likely to occur at meta position. Thus, —NO_2 group is meta directing so far as electrophilic ring substitution is concerned. Some examples are :



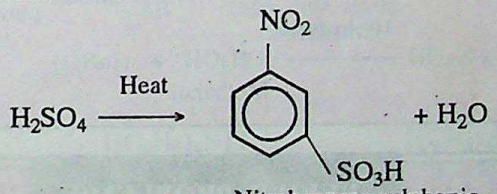
Nitrobenzene

Nitration



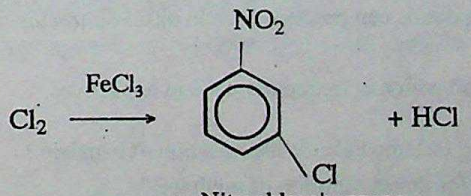
m-Dinitrobenzene

Sulphonation



m-Nitrobenzene sulphonic acid

Chlorination



m-Nitrochlorobenzene

Uses of Nitro Compounds

1. Nitro compounds are widely used as industrial solvents.

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2. They form starting material for the manufacture of primary amines, carboxylic acids and their derivatives.

3. They are intermediates in the production of explosives. For example, 2, 4, 6 trinitrotoluene (TNT) and 1, 3, 5-trinitrobenzene (TNB) are popular explosives.

4. Nitroarenes are also used for preparation of large number of aromatic compounds which are used in *dye stuffs, detergents, propellants and other pharmaceuticals.*

5. Chloropicrin is used as insecticide.

Distinction between Nitroalkanes and Alkyl nitrites

The two classes of compounds are functional isomers of each other :

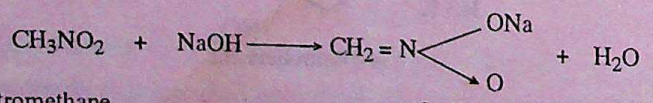
They can be distinguished on the basis of their specific chemical behaviour.

1. **Reduction.** Nitroalkanes on reduction with H_2/Ni produce *primary amines*, while alkyl nitrites on reduction produce *alcohols* and *ammonia*.

$$\underset{\text{Nitroethane}}{CH_3CH_2NO_2} \xrightarrow{6(H)} \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} + H_2O$$

$$\underset{\text{Ethylnitrite}}{CH_3CH_2O—N = O} \xrightarrow{6(H)} \underset{\text{Ethanol}}{CH_3CH_2OH} + NH_3 + H_2O$$

2. **Hydrolysis in Basic conditions.** Nitroalkanes do not get hydrolysed with NaOH but form salts. Nitrites, on the other hand, produce alcohols.



$$\underset{\text{Methyl nitrite}}{CH_3O—N = O} + NaOH \xrightarrow{\text{Hydrolysis}} \underset{\text{Methanol}}{CH_3OH} + NaNO_2$$

REVIEW PROBLEMS

9.6. Which reagents can be used to prepare chloropicrin ? **Ans.** *CH_3NO_2 and Cl_2/NaOH or $CHCl_3$ and HNO_3*

9.7. Which type of nitro compounds can produce pseudo nitrol on treatment with HNO_2 ? **Ans.** *Secondary nitroalkanes.*

9.8. Name any nitro compound which is frequently used in explosives. **Ans.** *Trinitrotoluene (TNT)*

9.9. Which ion is the attacking intermediate during nitration of benzene ? **Ans.** *$\overset{\oplus}{N}O_2$ (nitronium ion)*

9.10. Which technique is used for direct nitration of methane ? **Ans.** *Vapour phase nitration*

9.11. Which reagent will produce azoxy benzene from nitrobenzene ? **Ans.** *Na_3AsO_3/NaOH*

9.12. Which organic compound is formed when 2-nitropropane is hydrolysed with boiling dilute HCl. **Ans.** *Acetone*

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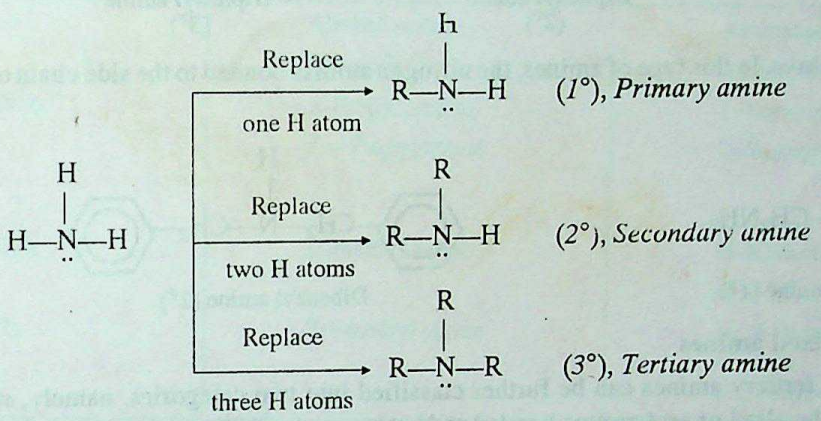
AMINES

Amines may be regarded as the alkyl or aryl derivatives of ammonia. They are obtained by the replacements of one or more hydrogen atoms of ammonia by alkyl or aryl groups. They can be classified into primary, secondary or tertiary amines, depending upon whether one, two or three H atoms of ammonia have been replaced by alkyl or aryl groups.



Thus, characteristic functional groups for *primary, secondary* or *tertiary* amines are :

$-\ddot{N}H_2$ (*p-amino*) $\quad$ $-\ddot{N}H-$ (*sec-amino*) $\quad$ $-\ddot{N}-$ (*tert-amino*)

respectively.

There is yet another class of compound besides these three types of amines, in which N atom is quaternary. Such compounds are called ***quaternary ammonium salts***. They are regarded as derivatives of ammonium salts in which all the four H atoms are replaced by alkyl or aryl groups.

$$\underset{\text{Ammonium halide}}{[NH_4]^+ \overset{-}{X}} \xrightarrow[+4R]{-4H} \underset{\text{Tetra alkyl ammonium halide}}{[NR_4]^+ \overset{-}{X}}$$

Some examples are

$[(C_2H_5)_4\overset{+}{N}]\overset{-}{Cl}$ Tetraethyl ammonium chloride $\quad$ $[(C_6H_5)_4\overset{+}{N}]\overset{-}{I}$ Tetraphenyl ammonium iodide $\quad$ $[(CH_3)_4\overset{+}{N}]\overset{-}{Br}$ Tetramethyl ammonium bromide

Classification of Amines

Amines are further classified broadly into two categories :

1. **Aliphatic amines.** In this type of amines, the nitrogen atom may be bonded to one or more alkyl chains. Some examples are :

CH_3NH_2 Methyl amine (1°) $\quad$ $CH_3-\overset{CH_3}{\overset{|}{N}}-H$ Dimethyl amine (2°) $\quad$ $CH_3-\overset{CH_3}{\overset{|}{N}}-CH_3$ Trimethyl amine (3°)

2. **Aromatic amines.** These can further classified into two types :

(*a*) **Aryl amines.** In this type of amines, the nitrogen atom is bonded to one or more aryl groups directly.

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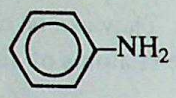
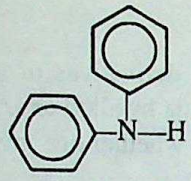
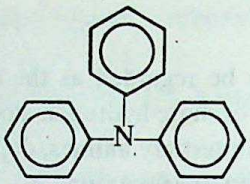


Aniline (1°)

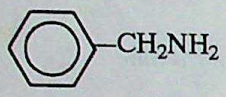


Diphenyl amine (2°)

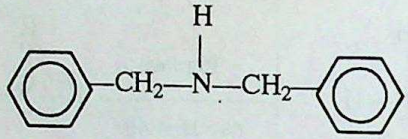


Triphenyl amine (3°)

(*b*) **Aralkyl amines.** In this type of amines, the nitrogen atom is bonded to the side chain of the aromatic systems.



Benzyl amine (1°)



Dibenzyl amine (2°)

Simple and Mixed amines

Secondary and tertiary amines can be further classified into two categories, namely, ***simple amines*** and ***mixed amines***. If the alkyl or aryl groups bonded to N atom are same, the amine is called **simple amine.** However, if alkyl or aryl groups bonded to the nitrogen atom are different, the amine is called **mixed amine.**

Simple amine : $C_2H_5—\overset{\overset{H}{|}}{N}—C_2H_5$ Diethyl amine

$C_6H_5—\overset{\overset{H}{|}}{N}—C_6H_5$ Diphenyl amine

$CH_3—\overset{\overset{CH_3}{|}}{N}—CH_3$ Trimethyl amine

Mixed amines : $C_2H_5—\overset{\overset{CH_3}{|}}{N}—H$ Ethyl methyl-amine

$C_6H_5—\overset{\overset{C_2H_5}{|}}{N}—H$ Ethylaniline

$CH_3—\overset{\overset{C_2H_5}{|}}{N}—C_3H_7$ Ethyl methyl propylamine

9.13. NOMENCLATURE

1. **Aliphatic amines. In common system,** the aliphatic amines are named by using prefix for alkyl group followed by the word *amine.*

In case of *mixed amines,* the names of alkyl groups are arranged in alphabetical order. This is followed by the word *amine.* However, for *simple* secondary or tertiary amines another prefix **di** or **tri** is added before the name of the alkyl group.

There is yet another system of naming amines according to which they are called **aminoalkanes.** In this system, the secondary or tertiary amines are named as **N-alkylaminoalkanes.** In this case, the smaller alkyl groups are taken as substituent on nitrogen atom. For example,

$CH_3—\overset{\overset{H}{|}}{N}—CH_3$ N-Methylaminomethane

$CH_3—\overset{\overset{H}{|}}{N}—C_2H_5$ N-Methylaminoethane

$CH_3—\overset{\overset{CH_3}{|}}{N}—CH_3$ N, N-Dimethyl aminomethane

$CH_3—\overset{\overset{C_2H_5}{|}}{N}—C_2H_5$ N-Ethyl-N-methyl aminoethane

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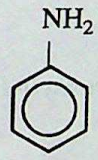
In **IUPAC system**, the amines are considered to be amino derivatives of corresponding alkanes. Therefore, they are called ***amino alkanes*** or ***alkanamines***. These names are obtained either by adding a prefix ***amino*** before the name of parent alkane or by replacing *e* from the name of the parent alkane with suffix ***amine***. The common and IUPAC names of some simple amines are given below in tabular form.

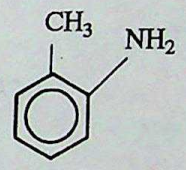
Amine	*Common name*	*IUPAC name*
CH_3NH_2	Methyl amine	Aminomethane or Methanamine
$CH_3CH_2NH_2$	Ethyl amine	Aminoethane or Ethanamine
$CH_3CH_2CH_2NH_2$	*n*-Propyl amine	1-Aminopropane or 1-Propanamine
$CH_3CH(NH_2)CH_3$	*Iso*-Propyl amine	2-Aminopropane or 2-Propanamine
$CH_3—NH—CH_3$	Dimethyl amine	N-Methylaminomethane or N-Methylmethanamine
$CH_3—N(CH_3)—CH_3$	Tri-methyl amine	N, N-Dimethyl aminomethane or N, N-Dimethylmethanamine

2. **Aromatic amines.** In **common system,** they are named by adding suffix *amine* to the name of aryl group. They may also be named as derivatives of simplest aromatic amine, *i.e., aniline.*

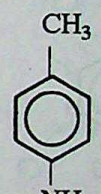
In **IUPAC** system, the simplest aromatic amine is called **benzenamine.** Other amines are named as derivatives of benzenamine. The common and IUPAC names of some aromatic amines are given below :



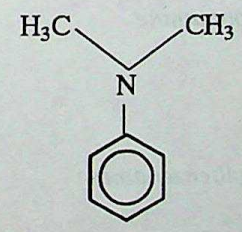
Aniline
(Benzenamine)



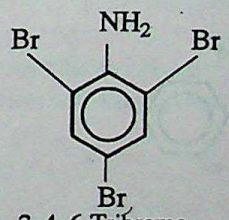
o-Toluidine or
2-Methylaniline
(2-Methylbenzenamine)



(*p*-Toluidine)
(4-Methylbenzenamine)



N, N-Dimethyl
aniline
(N, N-Dimethylbenzenamine)



2, 4, 6-Tribromo
aniline
(2, 4, 6-Tribromobenzenamine)

IUPAC names of some more complicated amines

(*i*) $CH_3CH_2CH(CH_3)CH_2CH_2—N(H)— CH_3$ — *3-Methyl-1-(N-methylamino) pentane* *Or* *3-Methyl-N-methyl-1-pentanamine*

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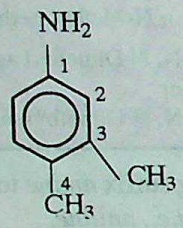
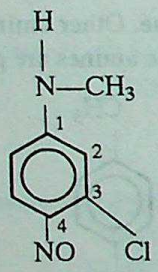
(*ii*) $CH_3CH_2CH_2-\underset{}{\overset{CH_3}{\overset{|}{N}}}-C_2H_5$ — *1-(N-Ethyl-N-methyl amino) propane*
Or
N-Ethyl-N-methyl-1-propanamine

(*iii*) $CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_2\overset{CH_3}{\overset{|}{C}}HCH_3$ (with NH_2 on the central CH) — *2, 5-Dimethyl-3-aminoheptane*
Or
2, 5-Dimethyl-3-heptanamine

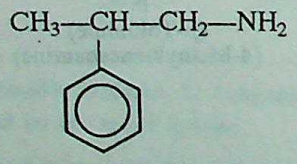
(*iv*) $(CH_3CH_2)_3N$ — *N-N-Diethyl aminoethane*
Or
N, N-Diethylethanamine

(*v*) 

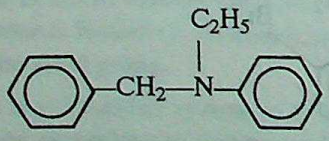
— *3, 4-Dimethylbenzenamine*

(*vi*) 

— *3-Chloro-4-nitroso-(N-methyl)-1-benzenamine*

(*vii*) 

— *2-Phenyl-1-propanamine*

(*viii*) 

— *N-Benzyl-N-ethylbenzenamine*

(*ix*) $CH_3CH_2\underset{\underset{CH_3}{|}}{\overset{N-H}{\overset{|}{CH}}}-CH_3$ — *2-(N-methyl amino) butane*
or
(N-methyl)-2-butanamine

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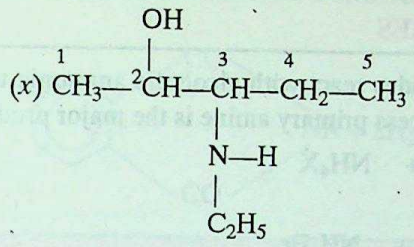
(x) 

3-(N-Methylamino)-2-pentanol

REVIEW PROBLEMS

9.13. Give structures and names of various amines represented by the formula C_3H_9N.

Ans. $CH_3CH_2CH_2NH_2$; *1-Propanamine (1°)*

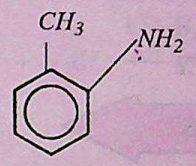
$CH_3CH(NH_2)CH_3$ *2-Propanamine (2°)*

$CH_3CH_2NH(CH_3)$ *N-Methylethanamine (2°)*

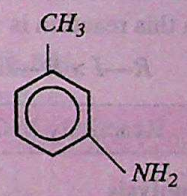
$CH_3N(CH_3)CH_3$ *N, N-Dimethyl methanamine (3°)*

9.14. Give the structure and names of various aryl as well as arylalkyl amines with formula C_7H_9N.

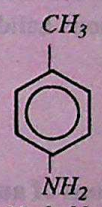
Ans.



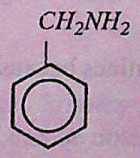
2-Methylbenzenamine



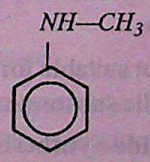
3-Methylbenzenamine



4-Methyl benzenamine



Phenyl methanamine



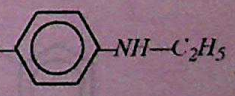
N-Methyl benzenamine

9.15. Give the structures of :

(*i*) 3-(N-Methylamino)-1-butanal (*ii*) 4-bromo-N-ethyl aniline

(*iii*) 2, 6-Diamino hexanoic acid (*iv*) 2-(N-Ethyl-N-methyl amino) propane

Ans. (*i*) $CH_3CH(NH-CH_3)-CH_2-CHO$

(*ii*) 

(*iii*) $H_2N-CH_2-CH_2-CH_2-CH_2-CH(NH_2)-COOH$

(*iv*) $CH_3-N(C_2H_5)-CH(CH_3)-CH_3$

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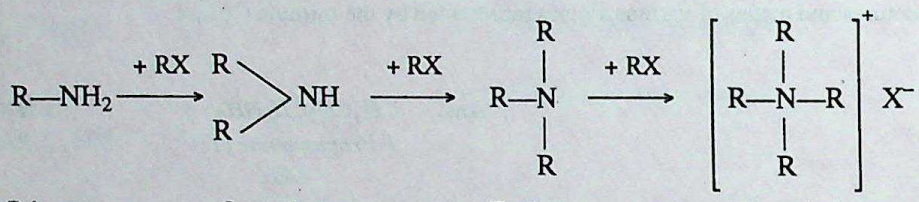
9.14. GENERAL METHODS OF PREPARATION OF AMINES

1. From Alkyl Halides. (*a*) **By ammonolysis.** Alkyl halides react with alcoholic ammonia to form primary, secondary and tertiary amines. If ammonia is used in excess primary amine is the major product.

$$\underset{\text{Alkyl halide}}{RX} + 2NH_3 \longrightarrow \underset{\text{Aminoalkane}}{RNH_2} + NH_4X$$

$$\underset{\text{Bromoethane}}{C_2H_5Br} + 2NH_3 \longrightarrow \underset{\text{Ethanamine}}{C_2H_5NH_2} + NH_4Br$$

If alkyl halide is in excess, the primary amine formed further reacts with alkyl halide to form secondary amine, tertiary amine and finally quaternary ammonium salt.



The composition of the final mixture depends upon the molar ratio of alkyl halide and ammonia at the beginning of the reaction. The above method is also known as **Hofmann's ammonolysis method.** The reactivity of various halides in this reaction is :

$$R—I > R—Br > R—Cl$$

Reactivity INCREASES

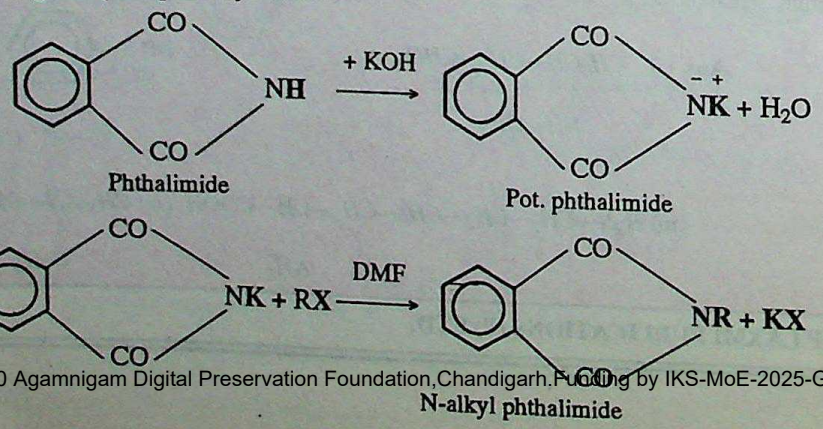
Limitations of ammonolysis

(*i*) Ammonolysis of alkyl halides does not give single amine but gives a mixture of primary, secondary and tertiary amines.

(*ii*) Ammonolysis is not suitable for preparing aryl amines because of the low reactivity of aryl halides towards nucleophilic substitutions.

(*b*) **Gabriel Phthalimide Synthesis**

Pure primary aliphatic amines are prepared from alkyl halides by **Gabriel phthalimide synthesis.** In this method phthalimide is first converted into potassium phthalimide by reaction with KOH. The potassium phthalimide on treatment with alkyl halide gives N-alkyl phthalimide which on hydrolysis with 20% hydrochloric acid gives pure primary amine.



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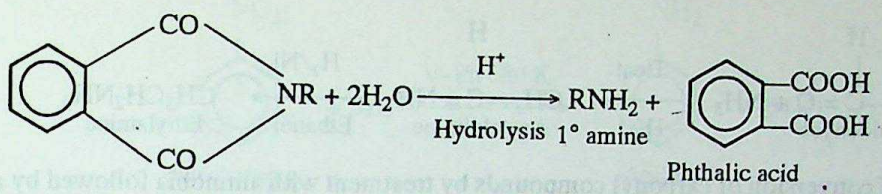
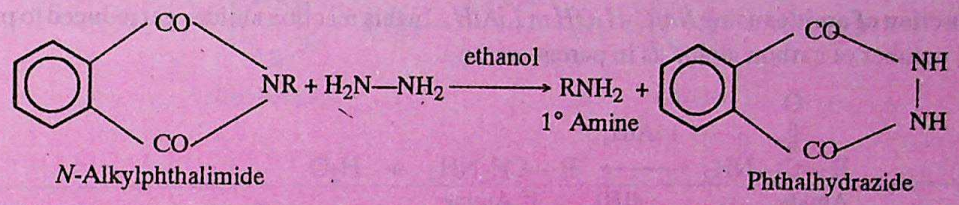


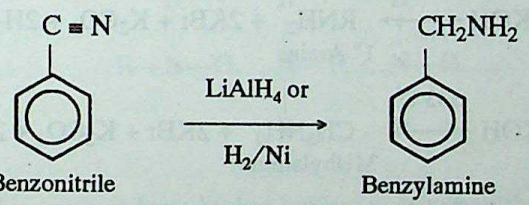
Hydrazinolysis (cleavage by using hydrazine) of N-alkyl phalimide is more efficient and effective method as *compared to hydrolysis* for getting *p*-amine in Gabriel synthesis



2. By Reduction of Alkyl Cyanides (*Mendius reaction*). The alkyl cyanides on reduction with H_2/Ni, $LiAlH_4$ or Na/C_2H_5OH give primary amines.

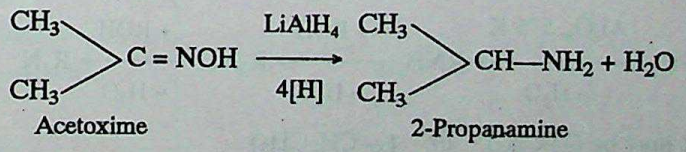
$$\underset{\text{Alkanenitrile}}{RCN} + 4H \xrightarrow[Na/C_2H_5OH]{LiAlH_4 \text{ or}} \underset{\text{Aminoalkane}}{RCH_2NH_2}$$

$$\underset{\text{Ethanenitrile}}{CH_3CN} + 4H \xrightarrow{LiAlH_4} \underset{\text{Aminoethane}}{CH_3CH_2NH_2}$$



3. By Reduction of Oximes. Primary amines can be prepared by the reduction of oximes with Na/C_2H_5OH or $LiAlH_4$. The oximes can be obtained from aldehydes and ketones by reaction with hydroxyl amines.

$$\underset{\text{Aldoxime}}{RCH = NOH} \xrightarrow[4[H]]{LiAlH_4} \underset{\text{Amine}}{RCH_2NH_2} + H_2O$$



4. By reductive amination of aldehydes or ketones. Aldehydes and ketones react with NH_3 to form imines which can be reduced by catalytic hydrogenation to primary amines.

$$\underset{\text{Aldehyde}}{R—\overset{H}{\overset{|}{C}}=O} + NH_3 \xrightarrow[-H_2O]{Heat} \underset{\text{Imine}}{R—\overset{H}{\overset{|}{C}}=NH} \xrightarrow{H_2/Ni} \underset{\text{1° Amine}}{R—CH_2NH_2}$$

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$$\underset{\text{Acetaldehyde}}{CH_3-\overset{\overset{H}{|}}{C}=O} + NH_3 \xrightarrow[-H_2O]{\text{Heat}} \underset{\text{Acetaldimine}}{CH_3-\overset{\overset{H}{|}}{C}=NH} \xrightarrow[\text{Ethanol}]{H_2/Ni} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

The process of conversion of carbonyl compounds by treatment with ammonia followed by reduction is called **reductive amination.** If we use 1°-amine in place of ammonia, it will yield 2° amine.

5. From Amides

(*a*) **By reduction of amides** using Na/C_2H_5OH or $LiAlH_4$. In this reaction amides get reduced to primary amines with same number of carbon atoms as in parent amide

$$\underset{\text{Amide}}{R-\overset{\overset{O}{||}}{C}-NH_2} \xrightarrow[4[H]]{LiAlH_4} \underset{1^\circ\text{ Amine}}{R-CH_2NH_2} + H_2O$$

$$\underset{\text{Ethanamide}}{CH_3-\overset{\overset{O}{||}}{C}-NH_2} \xrightarrow[4[H]]{LiAlH_4} \underset{\text{Ethanamine}}{CH_3CH_2NH_2} + H_2O$$

(*b*) **By Hoffmann's bromamide reaction.** Acid amides on reaction with Br_2 in the presence of alkalies at about 343 K give primary amines.

It may be noted that amine formed by this method has one carbon atom less than the parent compound.

$$\underset{\text{Amide}}{RCONH_2} + Br_2 + 4KOH \xrightarrow{343\text{ K}} \underset{1^\circ\text{ Amine}}{RNH_2} + 2KBr + K_2CO_3 + 2H_2O$$

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \xrightarrow{343\text{ K}} \underset{\text{Methylamine}}{CH_3NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} + Br_2 + 4KOH \xrightarrow{343\text{ K}} \underset{\text{Aniline}}{C_6H_5NH_2} + 2KBr + K_2CO_3 + 2H_2O$$

6. From alcohols (*Industrial method*). Aliphatic amines of low molecular mass are prepared on industrial scale by passing a mixture of an alcohol and ammonia in the vapour phase over heated alumina at 575 K. If ammonia is in excess, the primary amine is the major product. However, if the alcohol is in excess, then primary, secondary and tertiary amines are formed together.

$$ROH + NH_3 \xrightarrow[-H_2O]{Al_2O_3,\ 575\text{ K}} RNH_2 \xrightarrow[-H_2O]{+ROH} R_2NH \xrightarrow[-H_2O]{+ROH} R_3N$$

R may be $(-CH_3)$ or $(-CH_2CH_3)$

7. From nitro compounds. This involves the reduction of $-NO_2$ group either by catalytic hydrogenation (H_2/Pt or V) or by chemical means using Fe/HCl or Sn/HCl.

$$\underset{\text{Nitro alkane}}{R-NO_2} \xrightarrow[\text{Fe/HCl (6H)}]{3H_2/Ni\text{ or}} \underset{\text{Alkanamine}}{RNH_2} + 2H_2O$$

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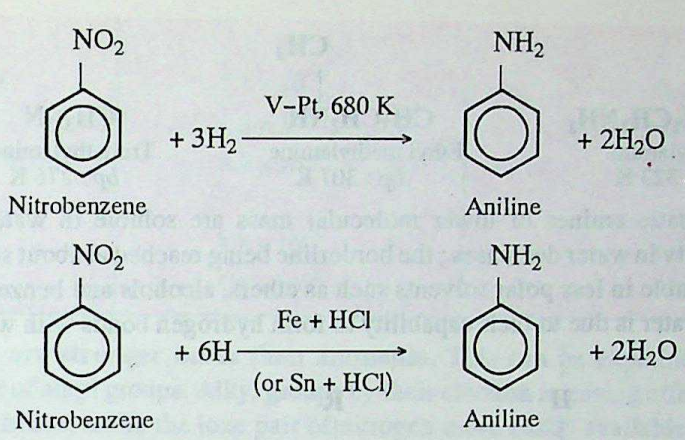


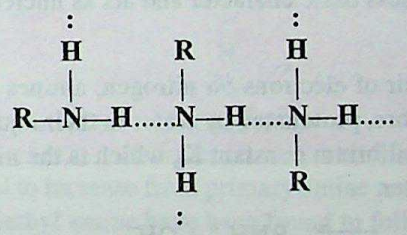
9.15. PHYSICAL PROPERTIES

1. Physical state and smell. Among aliphatic amines, the lower members are gases while higher members are liquids. Among arylamines the lower members are liquids while higher members are solids.

Methyl amine and ethyl amine have ammoniacal smell but higher amines have fishy small.

Most of the aromatic amines are colourless in pure form. However, they become coloured on keeping due to oxidation in air. Aromatic amines are generally toxic. They are easily absorbed through the skin.

2. Boiling points. All amines, except the tertiary amines are capable of forming intermolecular hydrogen bonds due to the presence of polar N—H bonds.



As a result of this, amines have higher boiling points than the non-polar compounds of comparable molecular masses. However, amines have lower boiling points than those of corresponding alcohols or carboxylic acids. This is due to the reason that O—H bond is more polar than N—H bond and hence hydrogen bonds in alcohols and carboxylic acids are stronger than the hydrogen bonds in amines.

Compounds	*Molecular mass*	*B.P. (K)*
$CH_3CH_2CH_3$ (propane)	44	231
CH_3OCH_3 (methoxymethane)	46	249
$CH_3CH_2NH_2$ (aminoethane)	**45**	**290**
CH_3CHO (ethanal)	44	293
CH_3CH_2OH (ethanol)	46	351
HCOOH (methanoic acid)	46	374

Among isomeric amines, the primary amines have highest boiling point due to more extensive H-bonding while tertiary amines have the least boiling point due to inability to form H-bonds. For example,

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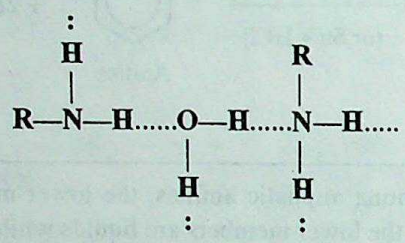
$CH_3CH_2CH_2NH_2$	$CH_3CH_2NH(CH_3)$	$(CH_3)_3N$
Propylamine	Ethyl methylamine	Trimethylamine
bp : 323 K	*bp* : 307 K	*bp* : 276 K

3. Solubility. Aliphatic amines of lower molecular mass are soluble in water. With increase in molecular mass, the solubility in water decreases ; the borderline being reached at about six carbon atoms. The higher amines are more soluble in less polar solvents such as ethers, alcohols and benzene. The solubility of lower aliphatic amines in water is due to their capability to form hydrogen bonds with water molecules.



Aromatic amines are insoluble in water but soluble in ether, alcohols and benzene.

9.16. CHEMICAL PROPERTIES

Like ammonia, the primary, secondary and tertiary amines all have a lone pair of electrons on nitrogen atom. As a result, the chemical behaviour of amines is very similar to that of ammonia. Due to the presence of lone pair of electrons, the amines possess basic character and act as nucleophiles in various reactions.

1. Basic Character

Due to the presence of a lone pair of electrons on nitrogen, amines are basic in character. They are stronger bases than water and are, therefore, protonated by water in their aqueous solutions. The basicities of amines are compared in terms of the equilibrium constant K_b which is the measure of the extent to which an amine can accept hydrogen ion from water.

$$RNH_2 + H_2O \rightleftharpoons RNH_3^+ + OH^-$$

$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

The equilibrium constant K_b is called **basicity constant.** Each amine has its characteristic K_b. The larger the value of K_b, the stronger is the base. A more convenient method of expressing the basic strength of amines is in terms of their pK_b values ($pK_b = -\log K_b$). Now, smaller the value of pK_b, more is the basic strength of amine. The K_b and pK_b values for some amines are given in Table 9.1.

Table 9.1. Basicity Constants of Some Amines

Compound	K_b	pK_b
Ammonia, NH_3	1.8×10^{-5}	4.7
1° Amines		
Methylamine, CH_3NH_2	4.4×10^{-4}	3.35
Ethylamine, $C_2H_5NH_2$	5.6×10^{-4}	3.2
Propylamine, $CH_3(CH_2)_2NH_2$	3.9×10^{-4}	3.4

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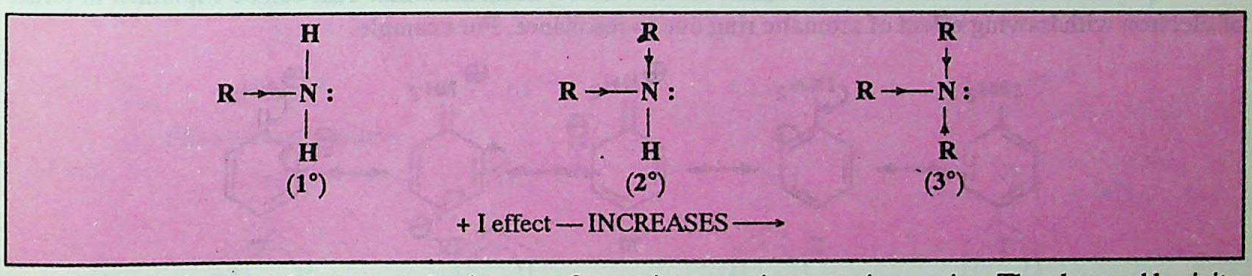
2° Amines		
Dimethylamine, $(CH_3)_2NH$	5.1×10^{-4}	3.29
Diethylamine, $(C_2H_5)_2NH$	1.3×10^{-3}	2.9
Dipropylamine, $(C_3H_7)_2NH$	8.2×10^{-4}	3.1
3° Amines		
Trimethylamine, $(CH_3)_3N$	5.3×10^{-5}	4.3
Triethyl amine, $(C_2H_5)_3N$	5.6×10^{-4}	3.2

(*i*) **Alkylamines are stronger bases than ammonia.** This can be explained in terms of *electron releasing inductive effect* of alkyl groups. Alkyl groups by their electron releasing effect, concentrate electron density on nitrogen and hence, make the lone pair of nitrogen more easily available for sharing with acids. Moreover, electron releasing effect of alkyl groups stabilizes the alkyl ammonium ion formed and hence, shifts the equilibrium in forward direction making the alkylamines stronger bases than ammonia.

$$R \rightarrow \ddot{N}H_2 + H_2O \rightleftharpoons R \rightarrow \overset{\oplus}{N}H_3 + \overset{-}{O}H$$

(*ii*) **Basic Strength of Primary, Secondary and Tertiary Alkylamines.** Among primary, secondary and tertiary aliphatic amines, the electron releasing effect is maximum in tertiary amines and minimum in primary amines.



The basic strength is expected to increase from primary amine to tertiary amine. The observed basicity of ethyl amine, diethyl amine and triethyl amine have been found to follow the expected order in **gas phase.** However, the order of basicity in aqueous solution does not follow the expected trend and gets altered as revealed by their K_b values (Table 9.1).

$$\underset{(2°)}{(C_2H_5)_2NH} > \underset{(1°)}{C_2H_5NH_2} > \underset{(3°)}{(C_2H_5)_3N}$$

BASIC CHARACTER DECREASES

Explanation

In fact, the basic strength in aqueous solutions depends not only upon electron releasing effect but also upon *steric effect* and *hydration effect.*

(*a*) **Steric effect** refers to the crowding of alkyl groups around N atom which hinders the attack of proton on the amine molecule and thus, decreases its basic strength. Since crowding of alkyl groups around N atom increases from primary to tertiary amines. Consequently basic strength of amines should decrease in the order 1° > 2° > 3°.

(*b*) **Hydration effect** refers to the stabilisation of the protonated amine by the water molecules. The water molecules form H-bonds with the protonated amine and release energy called hydration energy.

Now greater the extent of H-bonding in protonated amine more will be its stabilisation and consequently, greater will be the basic strength of the corresponding amine. The hydration due to H-bonding is maximum in monoalkyl ammonium ion (protonated cation of 1° amine), it is less in dialkyl ammonium ion and still less in trialkyl ammonium ion. Therefore, basic strength should decrease from 1° > 2° > 3°.

Thus, we find that in 3° amine hydration is least and steric hinderance is maximum. Thus, it is least basic inspite of maximum + I effect. In 1° amine steric hinderance is least and hydration is maximum but + I effect is also minimum.

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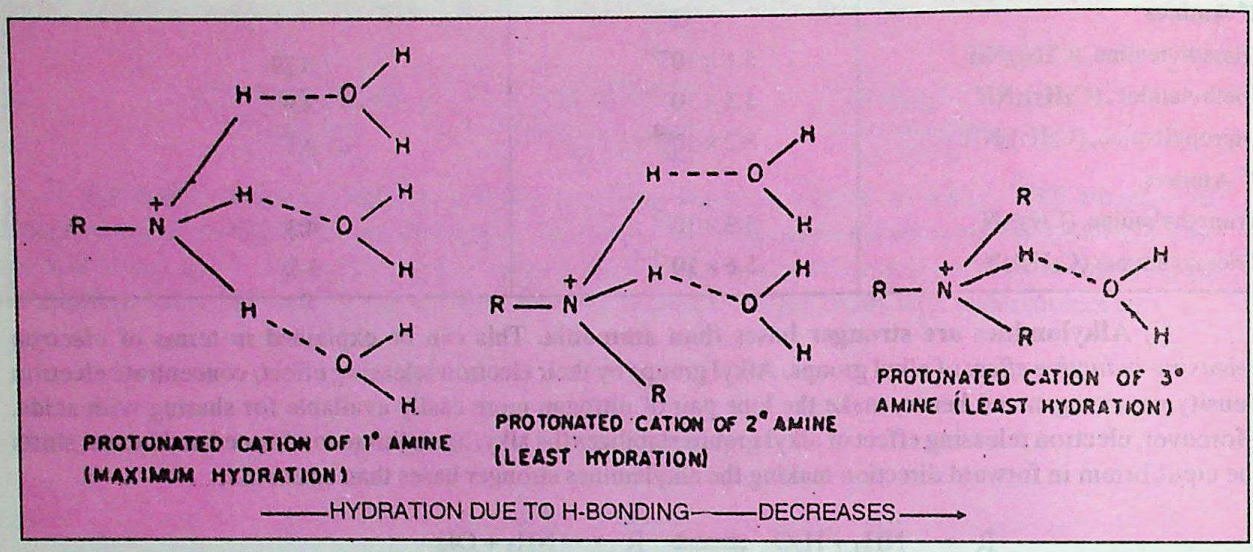
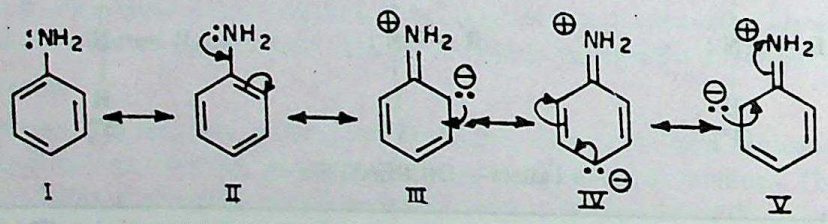


Hence its basic strength is more than 3° amine. The resultant of all factors cause 2° amine to be still more basic than 1° amine. Thus, overall basic strength varies as

$$2° > 1° > 3°$$

(*iii*) **Aromatic amines such as aniline are less basic than ammonia.** This can be explained in terms of electron withdrawing effect of aromatic ring due to resonance. For example.

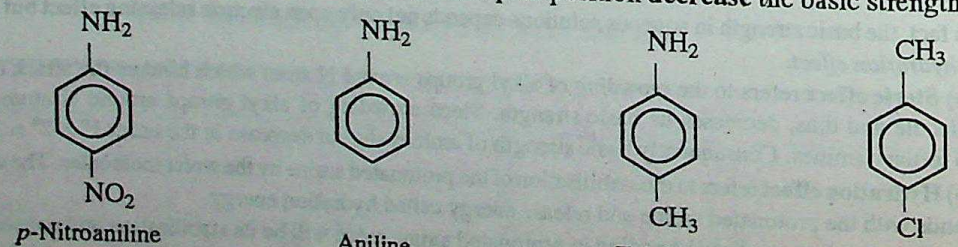


Aniline is resonance hybrid of the following contributing structures :

It is quite evident from the above resonating structures that the lone pair of electrons is withdrawn away from it and is being partially shared with benzene ring. Therefore, lone pair of nitrogen in aniline is not fully available for sharing with acids whereas in ammonia it is fully available for sharing. Hence, ***aniline is weaker base than aliphatic amines and ammonia.***

Effect of substituents on the Basic Character of Aromatic Amines

(*i*) The presence of **Electron releasing groups** such as **—OCH_3, —CH_3, —NH_2,** etc., at the para position **increases** the basic strength. On the other hand the presence of **Electron withdrawing** groups such as **—NO_2, —CN, —X,** etc., at the para position **decrease** the basic strength.



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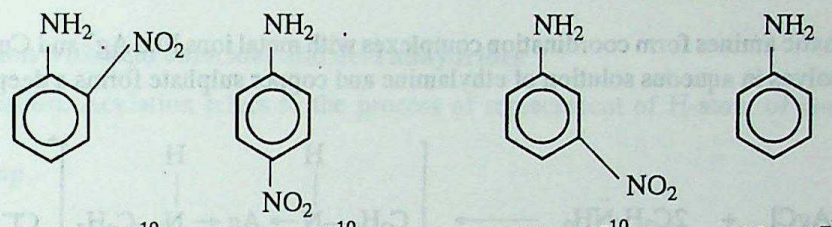
(*ii*) The base weakening effect of electron withdrawing groups and base strengthening effect of electron releasing groups in more marked at *p*-position in comparison to that in *meta positions.*

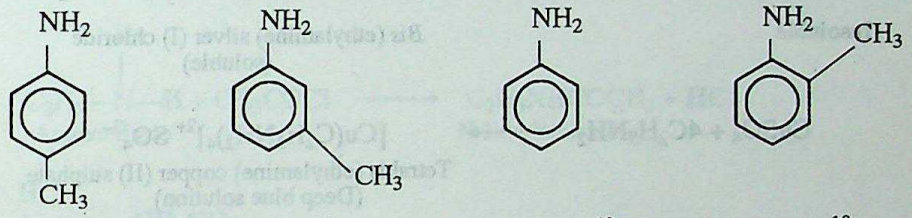
(*iii*) **Ortho effect.** The presence of electron releasing or electron withdrawing groups at the ortho positions causes **decrease** in the basic strength. This is called *ortho effect*. Some examples are given below.

(*a*) **Nitroanilines**



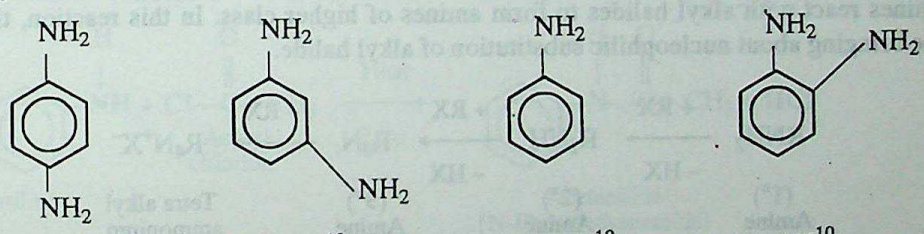
K_b : 0.00006×10^{-10} 0.001×10^{-10} 0.029×10^{-10} 4.2×10^{-10}

(*b*) **Toludines**



K_b : 12×10^{-10} 5×10^{-10} 4.2×10^{-10} 2.6×10^{-10}

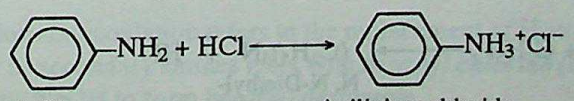
(*c*) **Phenylenediamines**



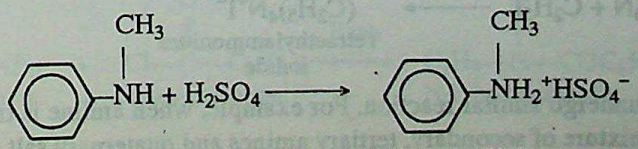
K_b : 140×10^{-10} 10×10^{-10} 4.2×10^{-10} 3×10^{-10}

Reaction in support of basic nature of amines. Amines react with aqueous solution of acids to form salts.

$$\underset{\text{Amine}}{RNH_2} + HCl \longrightarrow \underset{\text{Alkylammonium chloride}}{RNH_3^+Cl^-}$$



Aniline — Anilinium chloride (Aniline hydrochloride)



N-Methylaniline — N-Methylanilinium hydrogen sulphate

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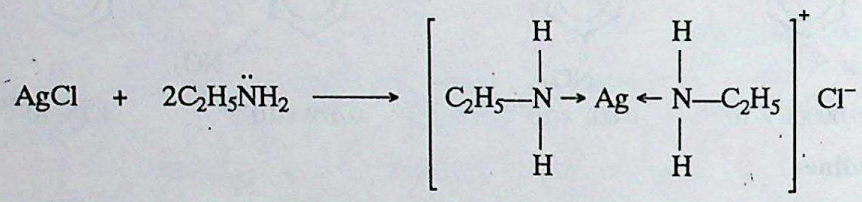
Salts of amines are typical ionic solids. They are non-volatile solids. On heating, these salts decompose before the melting point is reached. Amine salts are soluble in water but insoluble in non-polar solvents. A water insoluble amine can be separated from non-basic compounds by its solubility in aqueous solutions of acids. From the aqueous solution, the amine can be regenerated by making it alkaline.

2. Reaction with Metal Ions

Lower aliphatic amines form coordination complexes with metal ions like Ag^+ and Cu^{2+}. For example, silver chloride dissolves in aqueous solution of ethylamine and copper sulphate forms a deep blue solution.



Insoluble — *Bis* (ethylamine) silver (I) chloride (soluble)

$$CuSO_4 + 4C_2H_5\ddot{N}H_2 \longrightarrow [Cu(C_2H_5NH_2)_4]^{2+}\,SO_4^{2-}$$

Tetrakis (ethylamine) copper (II) sulphate (Deep blue solution)

3. Reaction with Alkyl Halides (*Alkylation*)

Amines react with alkyl halides to form amines of higher class. In this reaction, the amine acts as nucleophile bringing about nucleophilic substitution of alkyl halide.

$$\underset{\substack{(1^\circ)\\ \text{Amine}}}{RNH_2} \xrightarrow[-HX]{+RX} \underset{\substack{(2^\circ)\\ \text{Amine}}}{R_2NH} \xrightarrow[-HX]{+RX} \underset{\substack{(3^\circ)\\ \text{Amine}}}{R_3N} \xrightarrow{+RX} \underset{\substack{\text{Tetra alkyl}\\ \text{ammonium}\\ \text{halide}}}{R_4N^+X^-}$$

Since in this reaction hydrogen atoms attached to nitrogen in amines are substituted by alkyl groups, this reaction is referred to as **alkylation of amines.**

$$\underset{\text{Aminoethane}}{C_2H_5NH_2} + C_2H_5I \longrightarrow \underset{\substack{\text{N-Ethyl-}\\ \text{aminoethane}}}{(C_2H_5)_2NH} + HI$$

$$(C_2H_5)_2NH + C_2H_5I \longrightarrow \underset{\substack{\text{N, N-Diethyl-}\\ \text{aminoethane}}}{(C_2H_5)_3N} + HI$$

$$(C_2H_5)_3N + C_2H_5I \longrightarrow \underset{\substack{\text{Tetraethylammonium}\\ \text{iodide}}}{(C_2H_5)_4N^+I^-}$$

Aromatic amines also undergo similar reaction. For example, when aniline is treated with excess of methyl iodide under pressure, mixture of secondary, tertiary amines and quaternary salt are formed.

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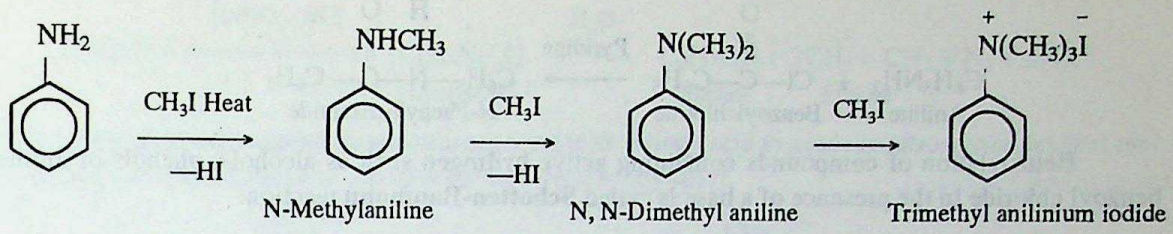
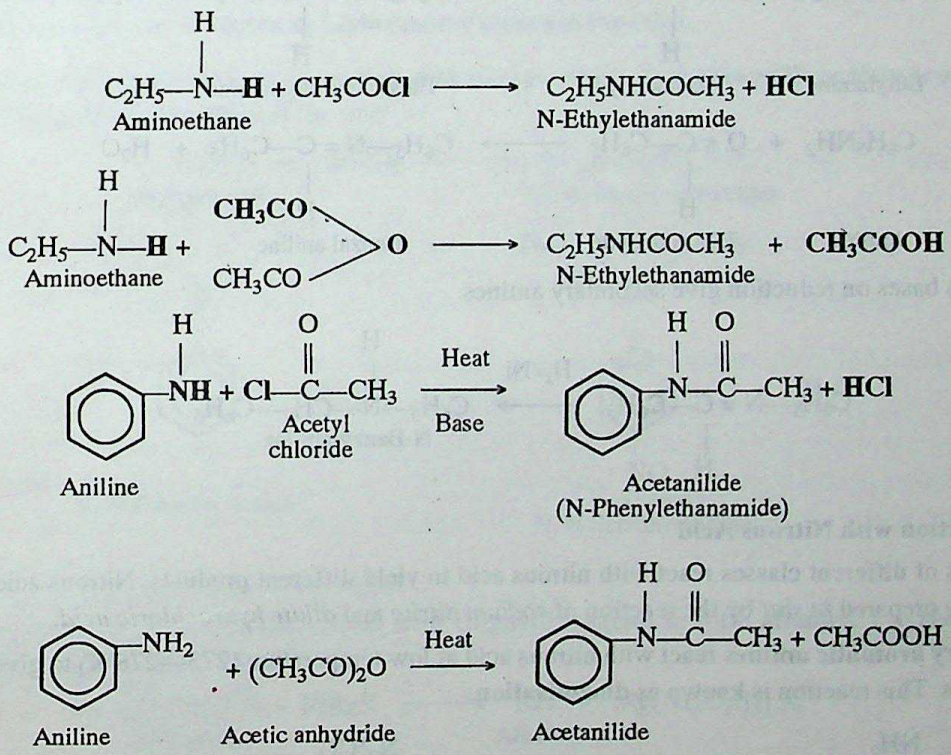


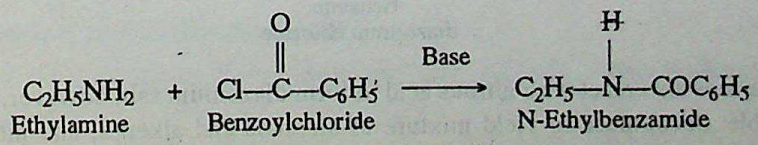
4. Reaction with acid chlorides and acid anhydrides

(*a*) **Acylation.** Acylation refers to the process of replacement of H-atom of amino group by acyl $\left(R-\underset{\underset{O}{\|}}{C}-\right)$ group.

Primary and secondary amines react with acid chlorides or acid anhydrides to form substituted amides. Tertiary amines do not undergo this reaction because they do not have H atom on the nitrogen.



(*b*) **Benzoylation.** Benzoylation refers to the replacement of H atom of amino group by benzoyl group (C_6H_5CO—). Primary or secondary amines react with ***benzoyl chloride (C_6H_5COCl)*** in the presence of a base like pyridine or aqueous NaOH to form benzoyl derivauve.



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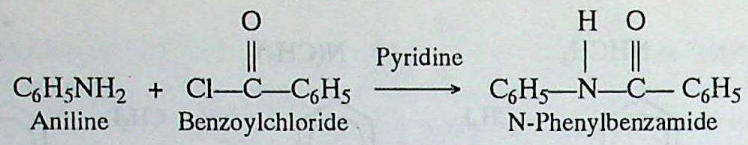
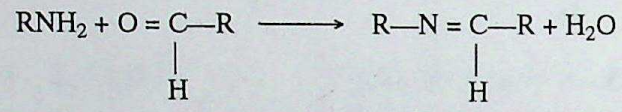


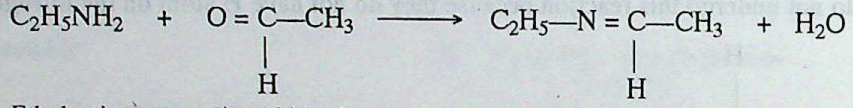
Benzoylation of compounds containing active hydrogen such as alcohols, phenols or amines with benzoyl chloride in the presence of a base is called **Schotten-Baumann** reaction.

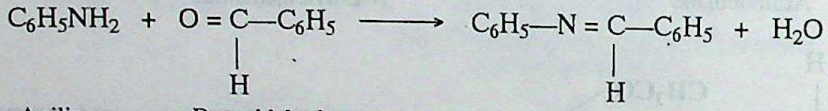
5. Reaction with aldehydes

Both aliphatic as well aromatic aldehydes react with primary amines to form **schiff's bases**, which are also called **anils.**

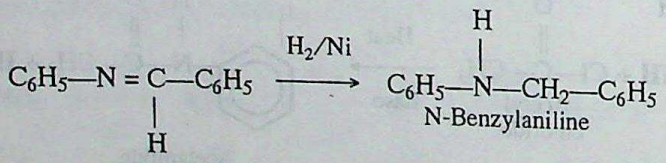


Schiff's base





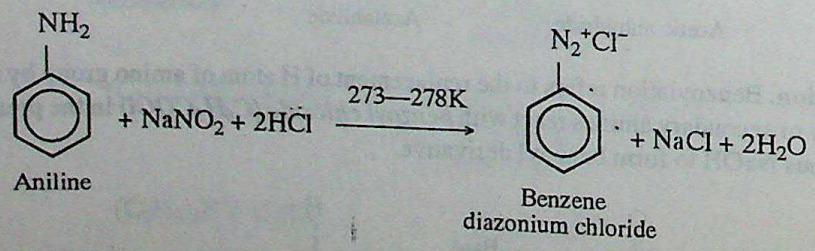
Schiff's bases on reduction give secondary amines



6. Reaction with Nitrous Acid

Amines of different classes react with nitrous acid to yield different products. Nitrous acid being an unstable acid is prepared *in situ* by the reaction of *sodium nitrite* and *dilute hydrochloric acid.*

Primary aromatic amines react with nitrous acid at low temperature (273—278 K) to give aromatic diazonium salts. This reaction is known as **diazotisation.**



Primary aliphatic amines also react with nitrous acid to form diazonium salt, however, the aliphatic diazonium salts being unstable, decompose to yield mixture of alcohols and alkenes, and nitrogen gas is evolved.

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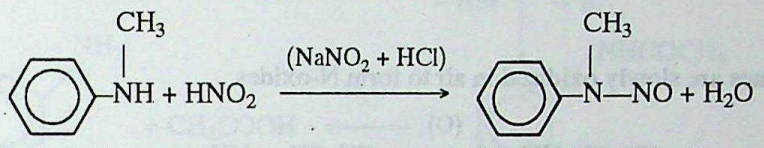
$$C_2H_5NH_2 \xrightarrow{NaNO_2/HCl} \underset{\text{(Unstable)}}{[C_2H_5\overset{+}{N}_2\overset{-}{Cl}]} \xrightarrow{H_2O} \underset{\text{Ethanol}}{C_2H_5OH} + \underset{\text{Ethene}}{2CH_2 = CH_2} + N_2 + 2H_2O$$

Secondary aliphatic and aromatic amines react with nitrous acid to produce nitroso-amines that are insoluble in the aqueous solution and separate out as a yellow oily layer.



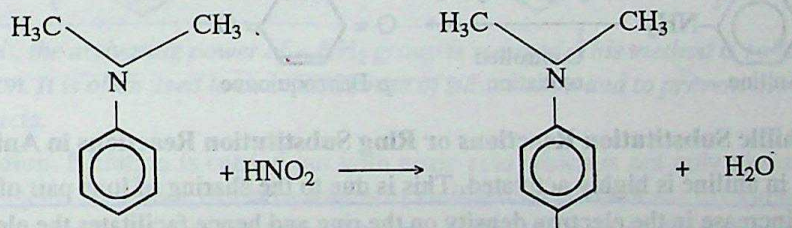
N-Methylaniline N-Nitroso-N-methylaniline

$$\underset{\text{Diethyl amine}}{(C_2H_5)_2NH} + HNO_2 \longrightarrow \underset{\text{N-Nitrosodiethylamine}}{(C_2H_5)_2N—NO} + H_2O$$

The nitrosoamines on warming with a little phenol and concentrated sulphuric acid produce **red** solution which turns **blue on** treatment with sodium hydroxide. This colour change provides an excellent test for secondary amines and is known as **Liebermann's nitroso reaction.**

Tertiary aliphatic amines on reaction with nitrous acid form nitrites while tertiary **aromatic amines** undergo electrophilic substitution at the ring.

$$\underset{\text{Triethyl amine}}{(C_2H_5)_3N} + HNO_2 \longrightarrow \underset{\text{Triethylammonium nitrite}}{[(C_2H_5)_3NH]^+NO_2^-}$$



N, N-Dimethylamine *p*-Nitroso N, N-dimethylaniline

7. Reaction with Grignard's reagent

Primary and secondary amines react with Grignard reagents to form **alkanes.** The *alkane is formed from alkyl* part of Grignard's reagent.

$$\underset{\text{Ethylamine}}{CH_3CH_2NH_2} + RMgX \longrightarrow \underset{\text{Alkane}}{RH} + Mg(NHC_2H_5)X$$

$$\underset{\text{Dimethyl amine}}{CH_3—\underset{\underset{CH_3}{|}}{N}—H} + C_2H_5MgBr \longrightarrow \underset{\text{Ethane}}{C_2H_6} + Mg[N(CH_3)_2]Br$$

8. Reaction with carbondisulphide

Primary amines react with CS_2 in the presence of $HgCl_2$ to give isothiocyanates.

$$CH_3CH_2NH_2 + CS_2 \xrightarrow{HgCl_2} \underset{\text{Ethyl isothiocyanate}}{CH_3CH_2—N = C = S} + HgS + 2HCl$$

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$$C_6H_5NH_2 + CS_2 \xrightarrow{HgCl_2} \underset{\text{Phenyl isothiocyanate}}{C_6H_5—N = C = S} + HgS + 2HCl$$

The isothiocyanates have characteristic smell like mustard oil, the reaction is called **Hofmann's mustard oil reaction.**

9. Oxidation

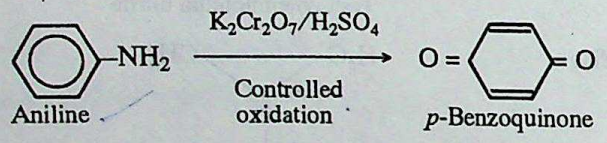
Aliphatic amines are slowly oxidised in air to form N-oxides.

$$CH_3CH_2NH_2 \xrightarrow{(O)} \underset{\text{Ethylamine N-oxide}}{CH_3CH_2—\underset{\underset{O}{\downarrow}}{NH_2}}$$

Aromatic amines are easily oxidised on explosure to air or on treatment with oxidants to form coloured complex compounds.

$$\textit{Aniline} \xrightarrow{K_2Cr_2O_7/H_2SO_4} \underset{\textit{(A black dye)}}{\textit{Aniline Black}}$$

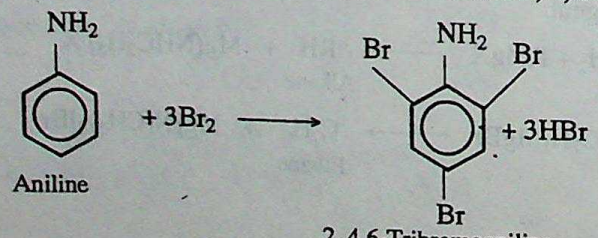
Controlled oxidation with $K_2Cr_2O_7$, however, gives *p*-benzoquinone



10. Electrophillic Substitution Reactions or Ring Substitution Reactions in Aniline

Benzene ring in aniline is highly activated. This is due to the sharing of lone pair of nitrogen with the ring which results in increase in the electron density on the ring and hence facilitates the electrophillic attack. The substitution-mainly takes place at *ortho* and *para* positions because electron density is more at ortho and para positions as is indicated by negative charge on ortho and para positions in the contributing structures (III, IV and V) of aniline (page 650).

(*a*) **Bromination.** Benzene ring in aniline is so activated that on reaction with aqueous bromine all the ortho and para positions get substituted resulting in the formation of 2, 4, 6-tri-bormoaniline.



To get a monobromo compound, the amino group is ***acetylated*** before bromination. After bromination, the bromoacetanilide is acid hydrolysed to yield the desired halogenated amine. Thus,

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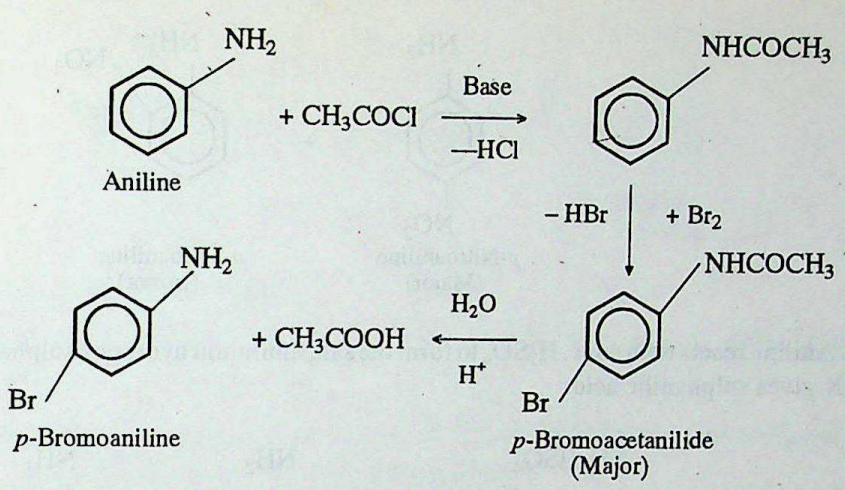
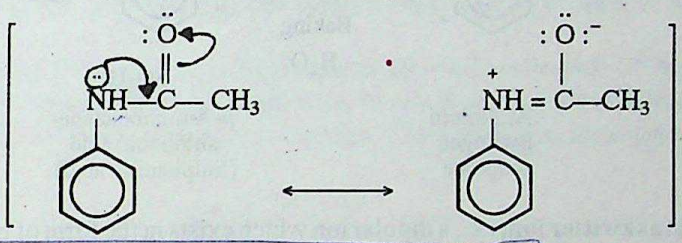
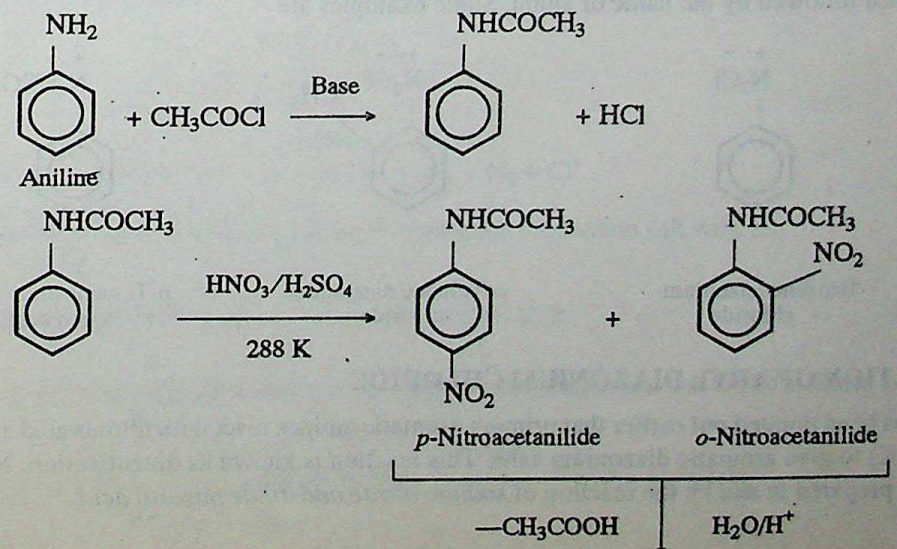


Purpose of acylation. *In acyl derivative of aniline, the electron pair of nitrogen is withdrawn towards carbonyl group as is shown by the following resonating structures :*



As a result, the activating power of —NH_2 group is reduced. This method is called protection of —NH_2 group by acylation. It is often used to control the rate of substitution and to prevent the formation of di and tri substituted products.

(*b*) **Nitration.** Nitration is carried out with nitric acid which is not only nitrating agent but is also a strong oxidizing agent. Therefore, direct treatment of aniline with HNO_3 leads to oxidation of highly activated benzene ring resulting in the formation of complex tarry oxidation products. Therefore, before nitration, aniline is first acetylated to protect —NH_2 group. Acetanilide on treatment with nitric acid in the presence of sulphuric acid gives *ortho* and *para* nitroacetanilide which on acidic hydrolysis give *ortho* and *para* nitroaniline.



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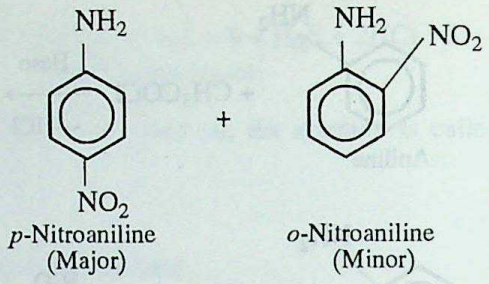
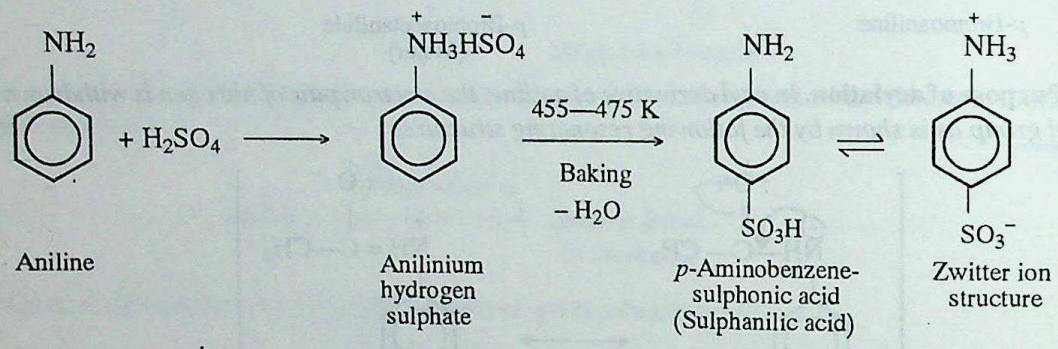


(*c*) **Sulphonation.** Aniline reacts with conc. H_2SO_4 to form the salt, anilinium hydrogen sulphate, which on '*baking*' at 455—475 K gives sulphanilic acid.

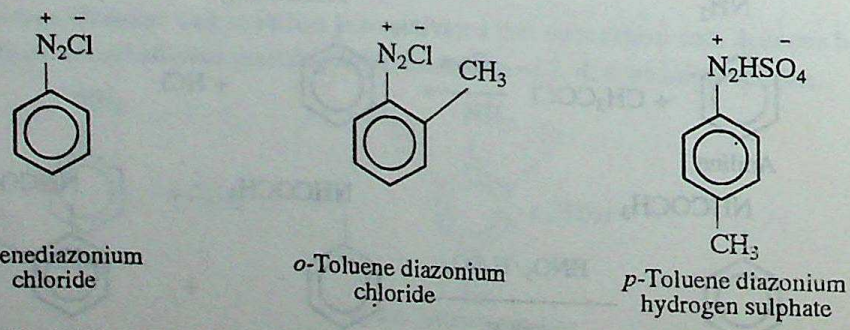


Sulphanilic acid exists as **zwitter ion,** *i.e.*, a dipolar ion which exists in the form of internal salt structure. Such ion has positive as well as negative charge within same molecular structure.

9.17. DIAZONIUM SALTS AND THEIR REACTIONS

The diazonium salts represented by the general formula $ArN_2^+X^-$ where X^- ion may be anion such as Cl^-, Br^-, HSO_4^-, etc. The $\overset{+}{N}_2$ group is $(\overset{+}{N} \equiv N)$ and is called diazonium group.

They are named by adding the word **diazonium** to the name of parent aromatic compound to which they are related followed by the name of anion. Some examples are



PREPARATION OF ARYL DIAZONIUM CHLORIDE

It has been pointed out earlier that primary aromatic amines react with nitrous acid at low temperature (273—278 K) to give aromatic diazonium salts. This reaction is known as **diazotisation.** Nitrous acid being unstable, is prepared *in situ* by the reaction of *sodium nitrite and dilute mineral acid.*

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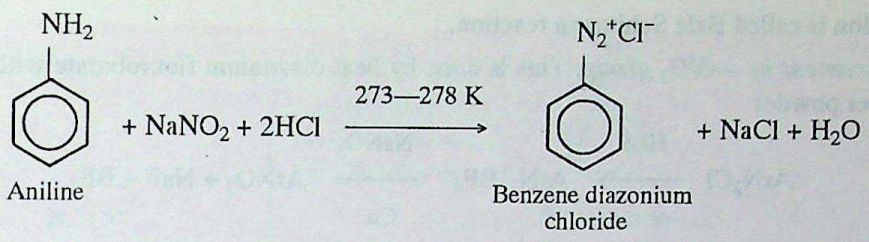

Reactions of Diazonium Salts

Aromatic diazonium salts undergo a large number of reactions. These reactions may be divided into two classes :

(*i*) *Replacement reactions* ; the reactions in which nitrogen is lost as N_2 and some other atom or group gets attached to the aromatic ring in its place.

(*ii*) *Coupling reactions* ; the reactions in which diazonium salt acts as electrophile and brings about substitution in some electron rich aromatic ring such as in phenols and in amines.

(*i*) **Replacement reactions.** (*a*) ***Replacement by —Cl, —Br and —CN.*** Aromatic diazonium salts on reaction with cuprous chloride give aryl chlorides, on reaction with cuprous bromide give aryl bromides and on reaction with cuprous cyanide give aryl cyanides. These reactions are known as **Sandmeyer's reactions.**

$$ArN_2^+Cl^- \xrightarrow{CuCl} ArCl + N_2$$

$$ArN_2^+Cl^- \xrightarrow{CuBr} AgBr + N_2 + Cl^-$$

$$ArN_2^+Cl^- \xrightarrow{CuCN} ArCN + N_2 + Cl^-$$

The arylchloride or bromides can also be prepared by **Gattermann reactions** which involve the treatment of diazonium salt with Cu/HCl or Cu/HBr respectively

$$ArN_2^+Cl^- \xrightarrow{Cu/HCl} ArCl + N_2$$

$$ArN_2^+Cl^- \xrightarrow{Cu/HBr} ArBr + N_2 + Cl^-$$

(*b*) ***Replacement by —I.*** This is done by warming the diazonium salt with KI.

$$ArN_2^+Cl^- + KI \xrightarrow{Warm} ArI + N_2 + KCl$$

(*c*) ***Replacement by —F.*** This involves the treatment of diazonium salt with fluoboric acid.

$$ArN_2^+Cl^- \xrightarrow[\text{(Fluoboric acid)}]{HBF_4} ArN_2^+BF_4^- \xrightarrow{heat} ArF + N_2 + BF_3$$

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The reaction is called Balz Schimann reaction.

(*d*) ***Replacement by —NO_2 group.*** This is done by heat diazonium flouroborate with $NaNO_2$ in the presence of copper powder

$$\overset{+\ -}{ArN_2Cl} \xrightarrow{HBF_4} ArN_2^+BF_4^- \xrightarrow[Cu]{NaNO_2} ArNO_2 + NaF + BF_3$$

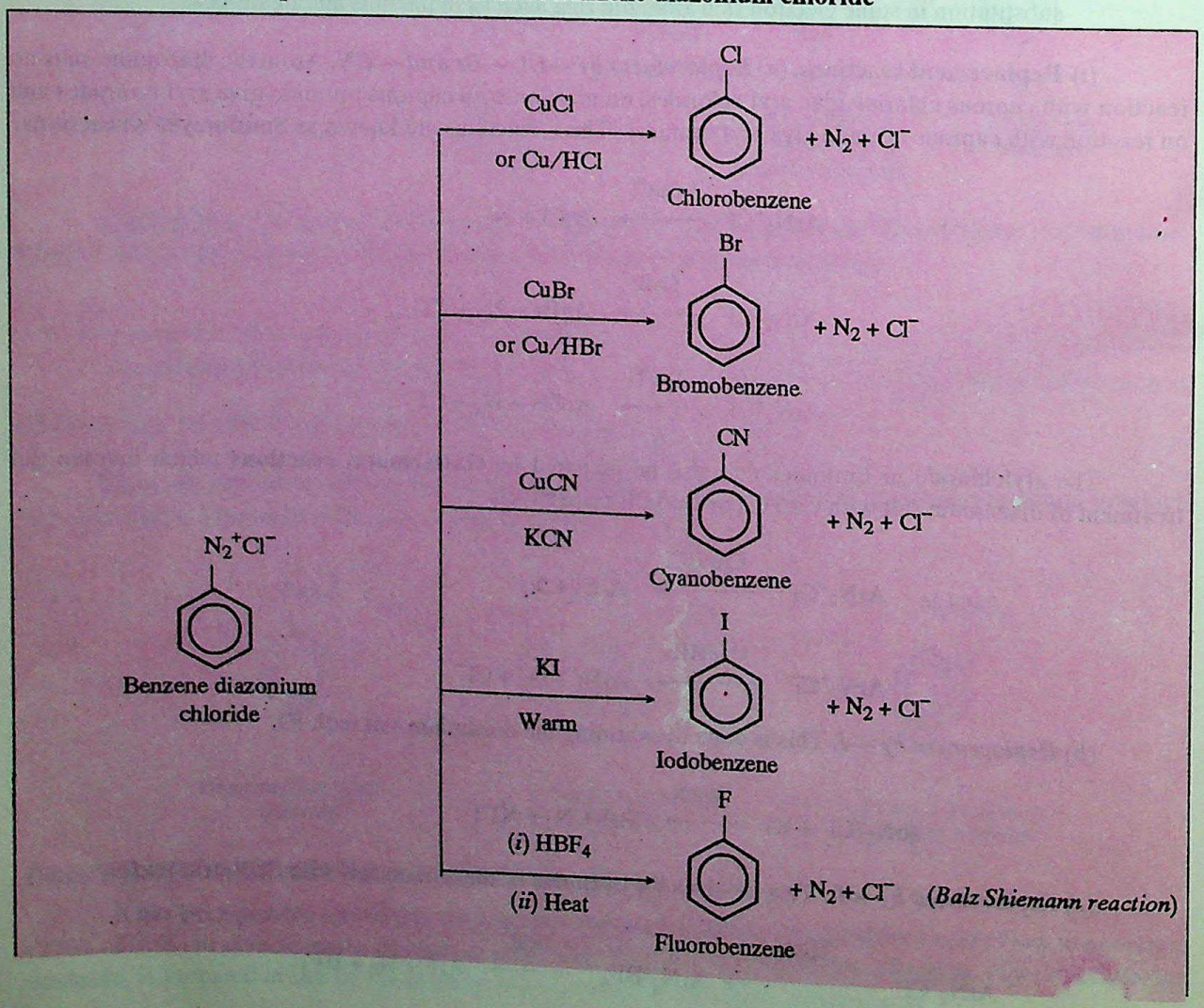
(*e*) ***Replacement by —OH.*** This involves warming the diazonium salt with water.

$$ArN_2^+Cl^- + H_2O \xrightarrow{H^+,\ Warm} ArOH + N_2 + HCl$$

(*f*) ***Replacement by H.*** This is done by treatment with hypophosphorus acid.

$$\underset{}{ArN_2^+Cl^-} + \underset{\text{Hypophosphorus acid}}{H_3PO_2} + H_2O \longrightarrow \underset{\text{Arene}}{ArH} + N_2 + H_3PO_3 + HCl$$

Summary of Replacement Reactions of Benzene diazonium chloride



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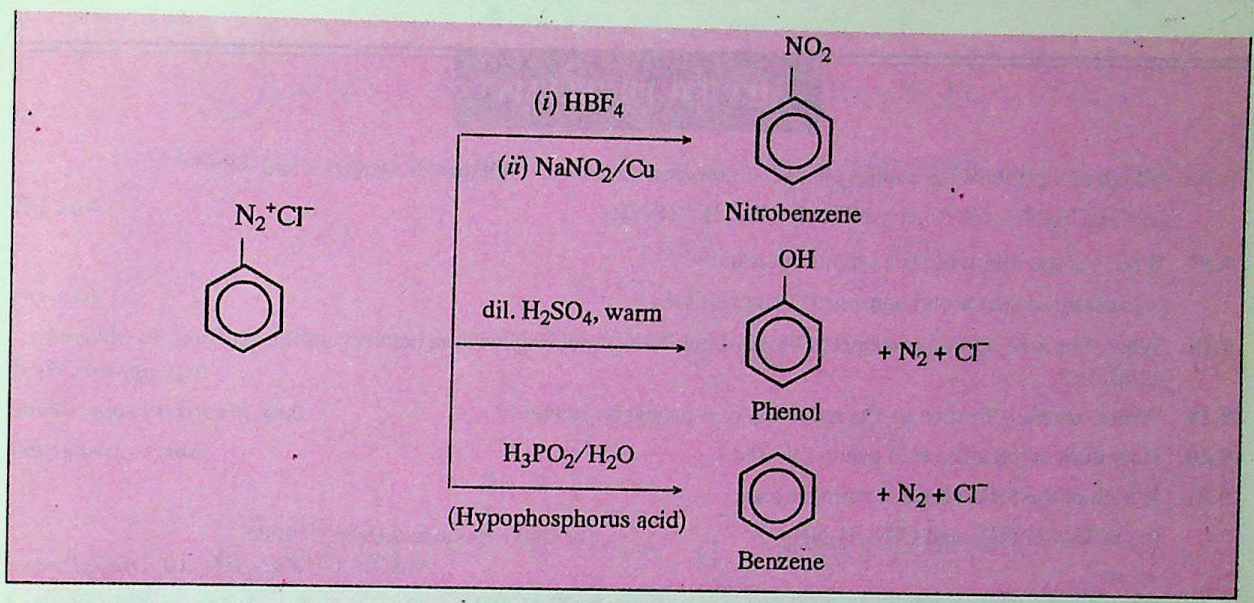
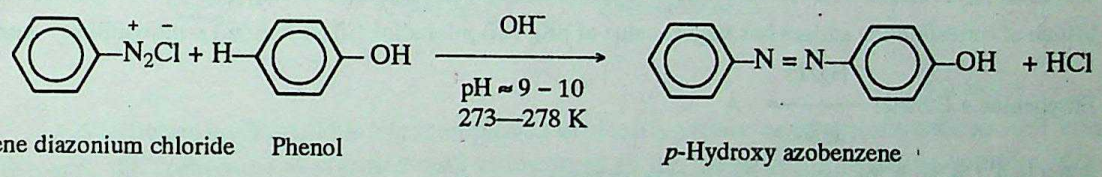
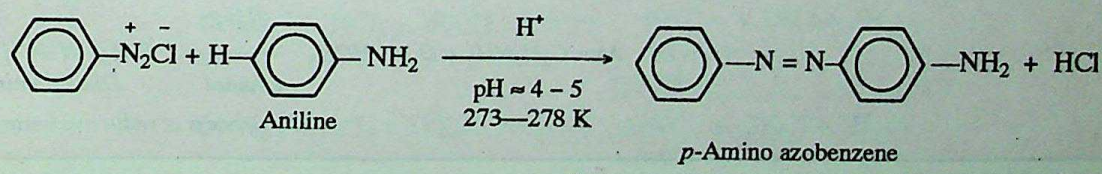


(*ii*) **Coupling reactions.** Diazonium salts react with highly activated aromatic compounds such as phenols and amines to form azo compounds. Azo compounds are coloured and many of them are used as dyes and indicators. The reaction with phenols takes place in slightly alkaline medium while with amines it occurs in slightly acidic medium.

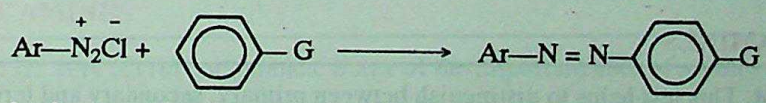
(*i*) *Reaction with phenol*



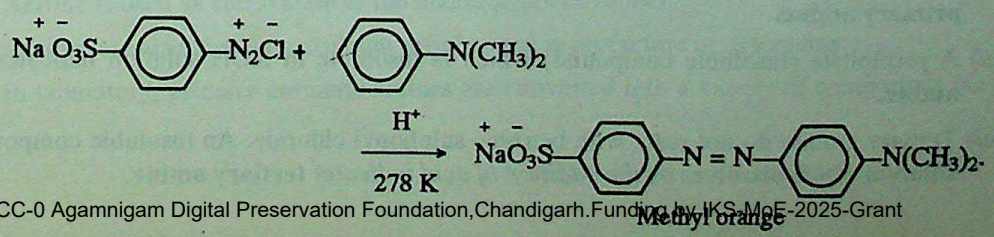
(*ii*) *Reaction with aniline*



In general, coupling reaction may be represented as



where, G is *strongly electron releasing group such* as — OH, —NH_2, —NHR, —NR_2 etc. For example, the acid-base indicator *methyl orange* is obtained by coupling of *diazonium salt of sulphanilic acid* and *N, N-dimethylaniline.*



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REVIEW PROBLEMS

9.16. Which of the following amines cannot be prepared by Gabriel Phthalimide synthesis and why ?

(*i*) $CH_3CH_2NH_2$ (*ii*) $(C_2H_5)_2NH$ (*iii*) $CH_3CH_2CH_2NH_2$ **Ans.** (*ii*)

9.17. Which of the following is a substituted amide ?

(*a*) acetanilide (*b*) acetyl benzene (*c*) ethylaniline **Ans.** (*a*)

9.18. What should be approximate pH of the medium during coupling reaction between aniline and benzene diazonium chloride ? **Ans.** *approx., 4—5*

9.19. Which amine is formed by the reduction of *n*-propyl isocyanide ? **Ans.** *Methyl n-propyl amine*

9.20. How does sulphanilic acid generally exist ? **Ans.** *as zwitter ion*

9.21. Which of the following is a stronger base ?

(*a*) $FCH_2CH_2NH_2$ and $CH_3CH_2NH_2$ (*b*) Ethyl amine and Diethylamine

Ans. (*a*) $CH_3CH_2NH_2$; (*b*) *Diethylamine*

9.22. What happens when 2-butanone oxime is treated with Na/C_2H_5OH ? **Ans.** *2-Butanamine is formed*

9.23. What is the IUPAC name of $CH_3—CH = CH—CH_2NH_2$? **Ans.** *But-2-en-1-amine*

9.24. How many isomeric amines with formula C_3H_9N are possible ? **Ans.** *Four isomeric amines are :*

(*i*) $CH_3CH_2CH_2NH_2$ (*ii*) $(CH_3)_2CHNH_2$
(*iii*) $CH_3CH_2NHCH_3$ (*iv*) $(CH_3)_3N$

9.25. Which isomeric amine with formula C_3H_9N is least basic and also has least boiling point ? **Ans.** $(CH_3)_3N$

9.26. Which of the following amines has largest value of pK_b ? (*i*) *p*-toludine (*ii*) aniline (*iii*) *p*-nitroaniline. **Ans.** (*iii*)

9.27. $$\text{Ethylamine + Ethanal} \xrightarrow[\text{Ethanol}]{H_2/Pt} A$$

What is A ? What is the name of the process we apply ?

Ans. $$C_2H_5NH_2 + O = CHCH_3 \xrightarrow[\text{ethanol}]{H_2/Pt} C_2H_5—\overset{\overset{H}{|}}{N}—CH_2CH_3$$

Diethylamine

The process is reductive amination.

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9.18. ANALYSIS OF AMINES

1. Hinsberg Test. This test helps to distinguish between primary, secondary and tertiary amines. The amine is treated with ***benzene sulphonyl chloride in the presence of excess of aqueous potassium hydroxide.***

(*i*) A clear solution in aqueous KOH which on acidification gives an insoluble material indicates **primary amine.**

(*ii*) A precipitate (insoluble compound) which is insoluble in KOH solution indicates **secondary amine.**

(*iii*) Tertiary amines do not react with benzene sulphonyl chloride. An insoluble compound in KOH solution which dissolves *by the addition of acid indicates* **tertiary amine.**

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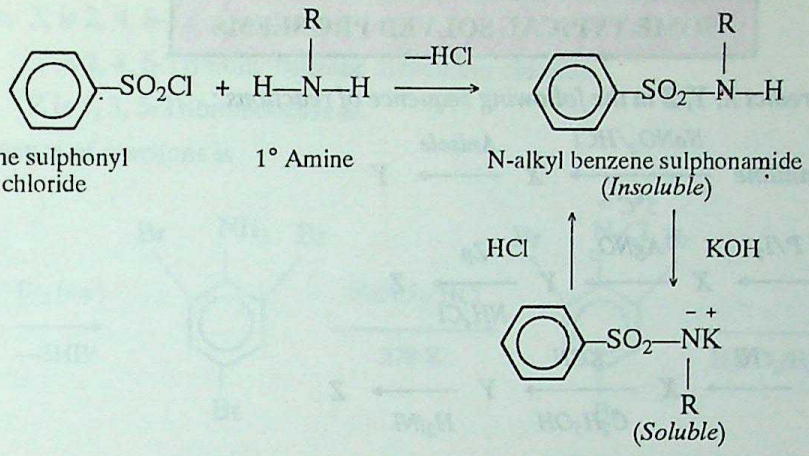

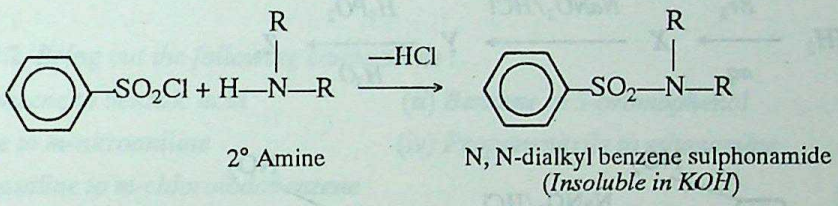

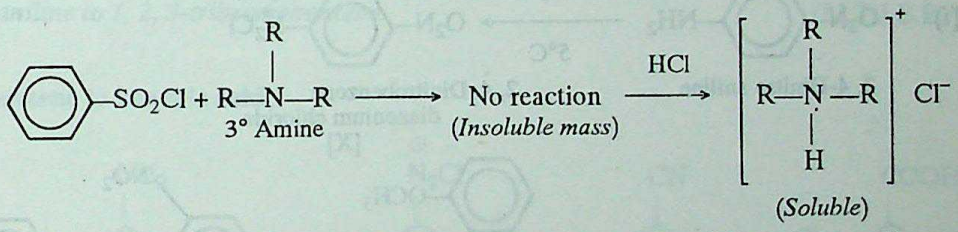

2. Carbylamine Test. This test is employed to identify *primary amines* (aliphatic as well as aromatic). In this test, the compound is warmed with chloroform in the presence of alcoholic solution of potassium hydroxide. The primary amines yield iso-cyanides which have an extremely unpleasant smell.

$$RNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Alkyl isocyanide}}{RNC} + 3KCl + 3H_2O$$

$$ArNH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Aryl isocyanide}}{ArNC} + 3KCl + 3H_2O$$

9.19. USES OF AMINES

Amines are very useful compounds. Some of the important uses of amines are given below :

1. Lower aliphatic amines are used as solvents.
2. Aniline and many other aromatic amines are used in the manufacture of dyes, indicators and drugs.
3. Aniline is used as antioxidant in the manufacture of rubber.
4. Amines are also used in petroleum refining and manufacture of detergents.
5. In laboratory, primary aromatic amines are converted into a variety of compounds *via* diazonium salts.

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SOME TYPICAL SOLVED PROBLEMS

Example 9.1. *Predict X, Y, Z in the following sequence of reactions :*

(*i*) *2, 4-Dinitroaniline* $\xrightarrow[5°C]{NaNO_2/HCl}$ $X \xrightarrow{Anisole} Y$ (I.I.T. 1995)

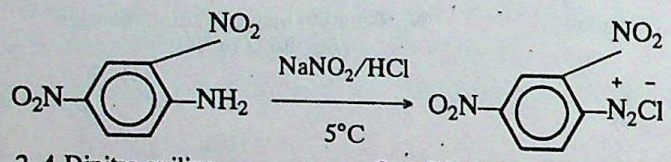
(*ii*) $C_2H_5OH \xrightarrow{P/I_2} X \xrightarrow{AgNO_2} Y \xrightarrow[NH_4Cl]{Zn} Z$

(*iii*) $CH_2 = CH_2 \xrightarrow{HI} X \xrightarrow[C_2H_5OH]{KCN} Y \xrightarrow[H_2/Ni]{} Z$

(*iv*) $C_6H_5NH_2 \xrightarrow[aq.]{Br_2} X \xrightarrow{NaNO_2/HCl} Y \xrightarrow[H_2O]{H_3PO_2} Z.$

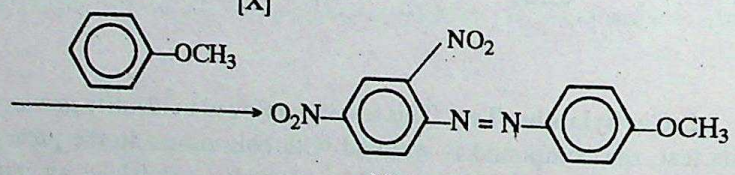
Solution.

(*i*)



2, 4-Dinitro aniline

2, 4, Dinitrobenzene diazonium chloride [X]



p-Methoxy, 2, 4-dinitro azobenzene

(*ii*) Here, X is C_2H_5I (Ethyl iodide),
Y is $C_2H_5NO_2$ (Nitroethane) and
Z is C_2H_5NHOH (Ethyl hydroxylamine)

The sequence of reactions is

$$C_2H_5OH \xrightarrow[-H_3PO_3]{P/I_2} C_2H_5I \xrightarrow[-AgI]{AgNO_2} C_2H_5NO_2 \xrightarrow[2[H]]{Zn/NH_4Cl} CH_3CH_2-\overset{\overset{H}{|}}{N}-OH$$

Ethylhydroxylamine

(*iii*) Here, X is C_2H_5I (Ethyl iodide)
Y is C_2H_5CN (Propanenitrile)
Z is $CH_3CH_2CH_2NH_2$ (1-Propanamine)

The sequence of reactions is

$$CH_2 = CH_2 \xrightarrow{HI} CH_3CH_2I \xrightarrow[C_2H_5OH]{KCN} CH_3CH_2CN \xrightarrow{H_2/Ni} CH_3CH_2CH_2NH_2$$

1-Propanamine

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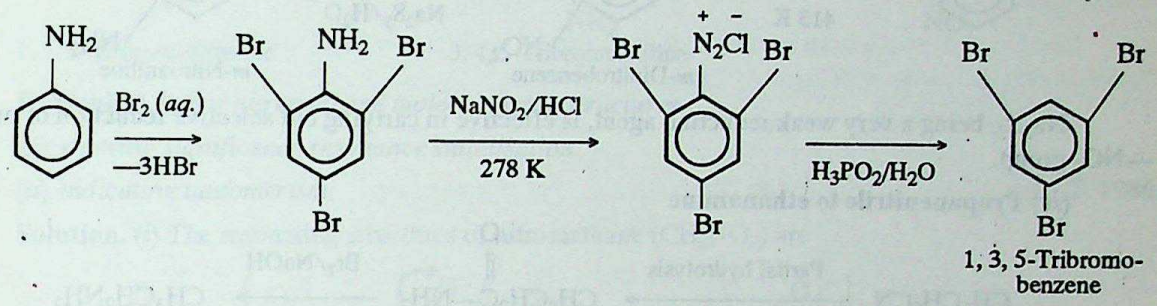
(*iv*) Here, X is 2, 4, 6-Tribromoaniline

Y is 2, 4, 6-Tribromobenzene diazonium chloride

Z is 1, 3, 5-Tribromobenzene.

The sequence of reactions is



Example 9.2. *Bring out the following conversions* :

(*i*) *Nitrobenzene to benzoic acid* (*ii*) *Benzene to 3-bromophenol*

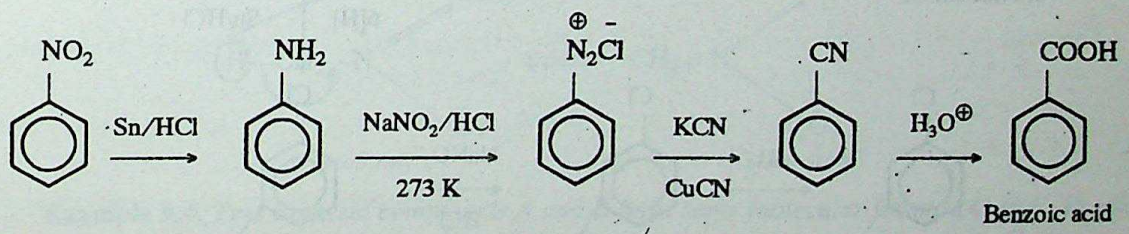
(*iii*) *Benzene to m-nitroaniline* (*iv*) *Propanenitrile to ethanamine*

(*v*) *m-nitroaniline to m-chloroiodobenzene* (Roorkee 1988)

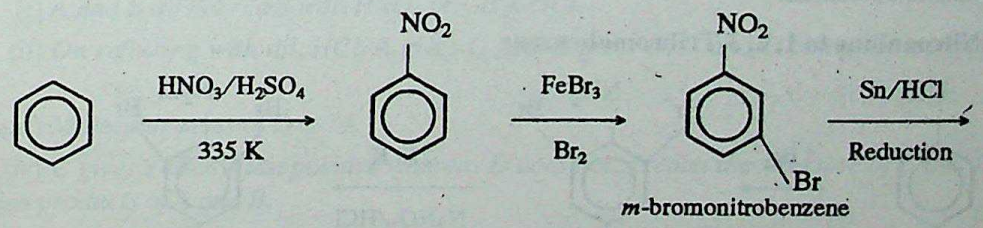
(*vi*) *4-nitroaniline to 1, 2, 3-tribromobenzene.* (I.I.T.J.E.E. 1990)

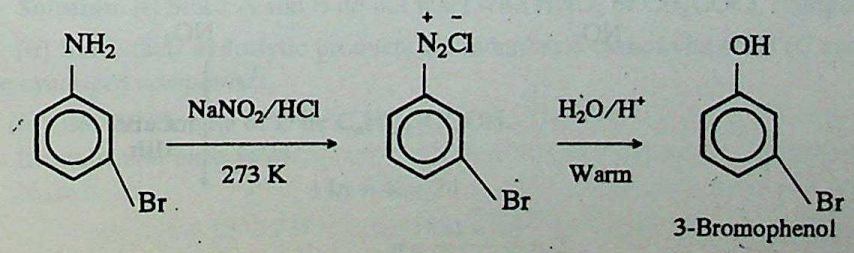
Solution.

(*i*) **Nitrobenzene to benzoic acid**



(*ii*) **Benzene to 3-bromophenol**





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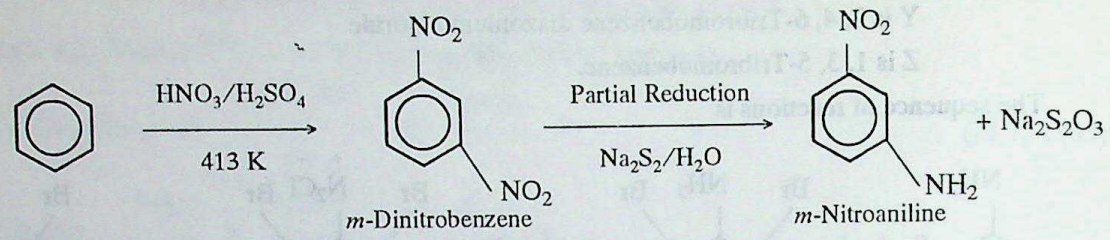
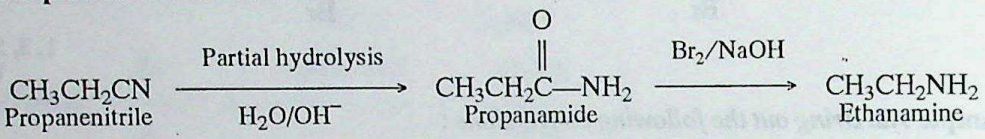
(*iii*) **Benzene to m-nitroaniline**

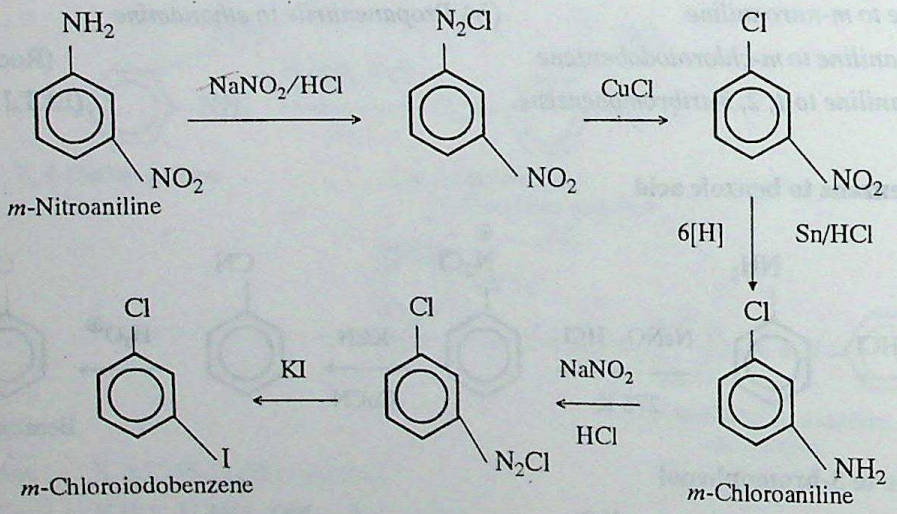


Na_2S_2, being a very weak reducing agent, is effective in carrying out selective reduction of only one —NO_2 group.

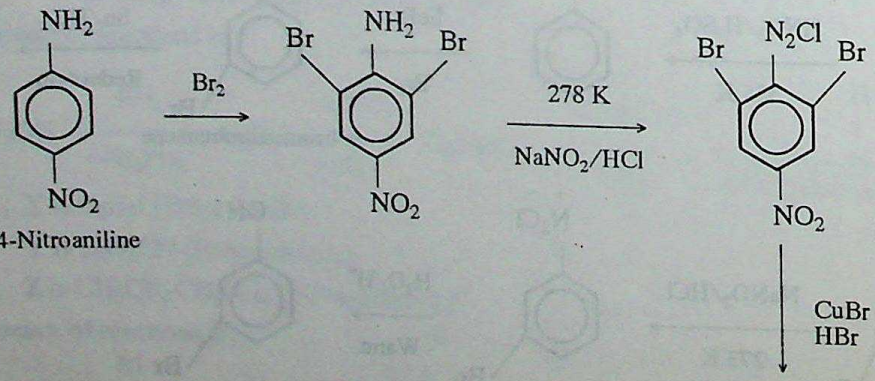
(*iv*) **Propanenitrile to ethanamine**



(*v*) **m-Nitroaniline to m-chloroiodobenzene**



(*vi*) **4-Nitroaniline to 1, 2, 3-Tribromobenzene**



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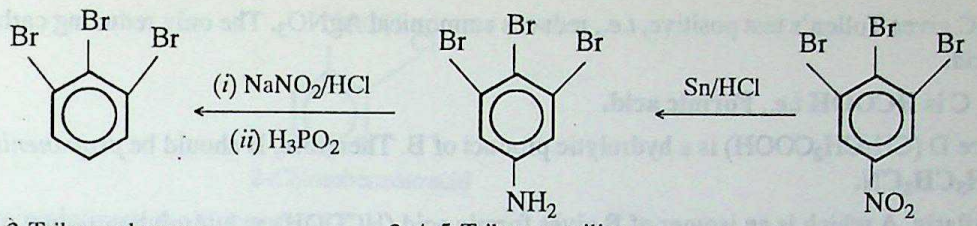


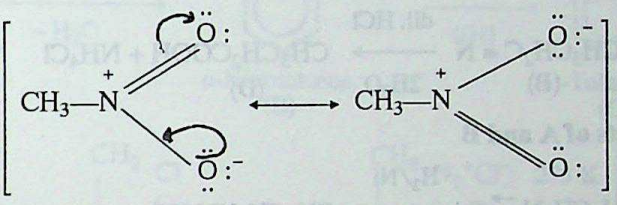
1, 2, 3-Tribromobenzene 3, 4, 5-Tribromoaniline

Example 9.3. *For nitromethane molecule write structures :*

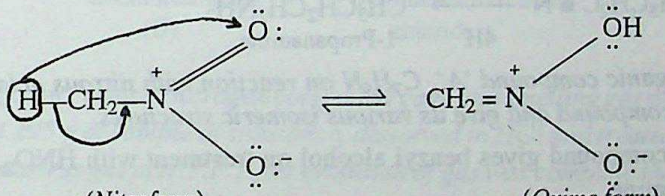
(*i*) *showing significance resonance stabilisation.*

(*ii*) *indicating tautomerism.* (I.I.T. 1986)

Solution. (*i*) The resonating structures of nitromethane (CH_3NO_2) are :



(*ii*) **Tautomerism** is kind of structural isomerism in which the isomers exist in dynamic equilibrium with each other and differ in electronic arrangement as well in the position of an atom/group. The isomers are called **tautomers.** The tautomeric forms of nitromethane are



(*Nitroform*) (*Oxime form*)

Example 9.4. *Two isomeric compounds A and B have same molecular formula C_3H_5N. Predict the structure of A and B on the basis of following informations :*

(*i*) *A and B do not react with HNO_2 or CH_3COCl.*

(*ii*) *On refluxing with dil. HCl, A gives C, and B gives D. C and D being the monobasic carboxylic acids.*

(*iii*) *Molecular mass of D is 74.*

(*iv*) *C gives Tollen's test positive whereas D does not. Predict the structure of C and D. Also give the reduction products of A and B.*

Solution. (*i*) Since A and B do dot react with HNO_2 or CH_3COCl, it implies that they are not *amines.*

(*ii*) Since their hydrolytic products are monobasic carboxylic acids (C and D), it means that A and B may be *cyanogen compounds.*

(*iii*) Let the formula of D be $C_nH_{2n+1}COOH$.

Its molecular mass is 74.

Now, $14n + 46 = 74$

$$n = \frac{74 - 46}{14} = 2$$

$\therefore$ D is C_2H_5COOH *i.e.*, **Propanoic acid**

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(*iv*) C gives Tollen's test positive, *i.e.*, reduces ammonical $AgNO_3$. The only reducing carboxylic acid is formic acid.

∴ C is **HCOOH** *i.e.*, **Formic acid.**

Since D (CH_3CH_2COOH) is a hydrolytic product of B. Therefore, **B** should be *propanenitrile* having formula $\mathbf{CH_3CH_2CN}$.

Similarly, **A** which is an isomer of **B** gives formic acid (HCOOH) as hydrolytic product, therefore, **A** should be *ethylisonitrile* with formula $\mathbf{CH_3CH_2N \overset{\rightarrow}{=} C}$.

The chemical equations are

$$\underset{(A)}{CH_3CH_2N \overset{\rightarrow}{=} C} \xrightarrow[2H_2O]{\text{dil. HCl}} CH_3CH_2NH_2 + \underset{(C)}{HCOOH}$$

$$\underset{(B)}{CH_3CH_2C \equiv N} \xrightarrow[2H_2O]{\text{dil. HCl}} \underset{(D)}{CH_3CH_2COOH} + NH_4Cl$$

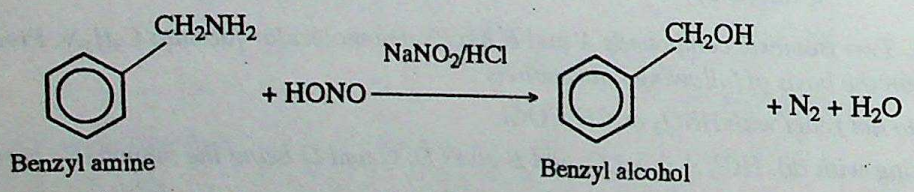
Reduction products of A and B

$$\underset{(A)}{CH_3CH_2N \overset{\rightarrow}{=} C} \xrightarrow[4H]{H_2/Ni} \underset{\text{N-Methyl ethanamine}}{CH_3CH_2NHCH_3}$$

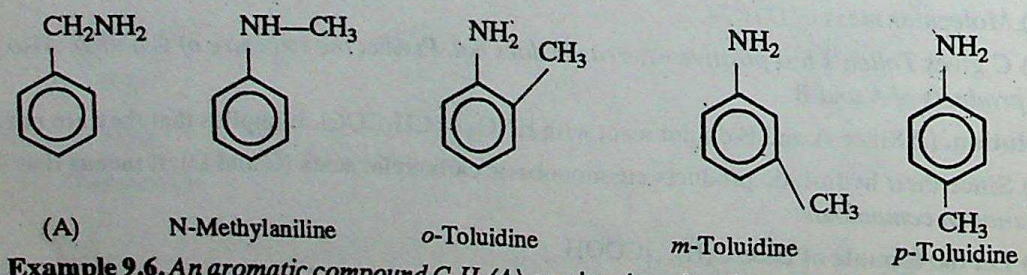
$$CH_3CH_2C \equiv N \xrightarrow[4H]{H_2/Ni} \underset{\text{1-Propanamine}}{CH_3CH_2CH_2NH_2}$$

Example 9.5. *An organic compound 'A', C_7H_9N on reaction with nitrous acid gave benzyl alcohol. Predict the structure of the compound and give its various isomeric structures.*

Solution. Since the compound gives benzyl alcohol on treatment with HNO_2. This implies that the compound must be benzyl amine.



The various isomeric structure, of the compound 'A' are :



Example 9.6. *An aromatic compound C_7H_8(A) on nitration gives B as a major product. B on reduction with Sn/HCl gives C. C on treatment with $NaNO_2$/HCl at 273 K followed by subsequent treatment with CuCl/HCl gives D. When D is oxidised, it forms ortho substituted monocarboxylic acid with formula $C_7H_5O_2Cl$. Predict the structures of A, B, C, D.*

Solution. D is an ortho substituted monocarboxylic acid. It means it contains —COOH and a chloro group at the ortho position. Therefore its formula is

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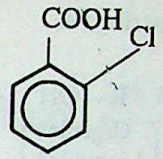
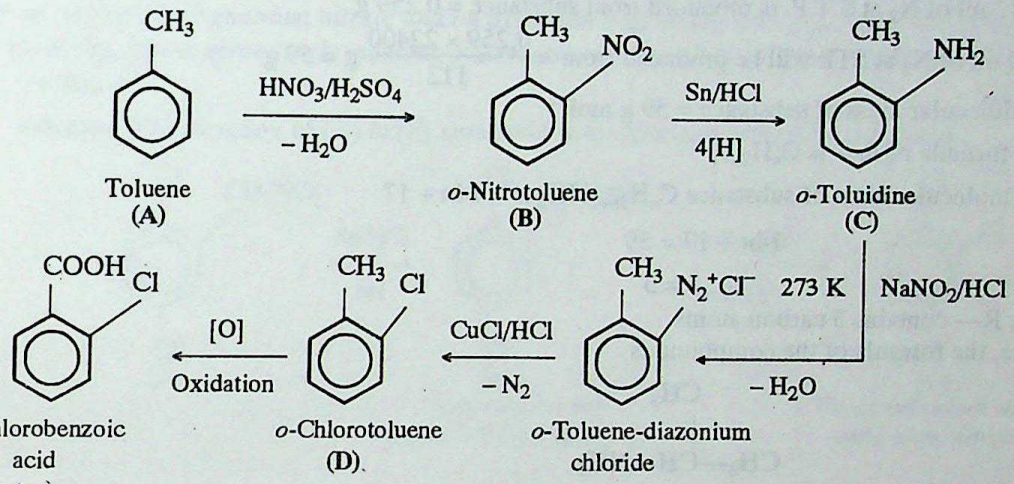


2-Chlorobenzoic acid

Keeping in mind the structure of D.

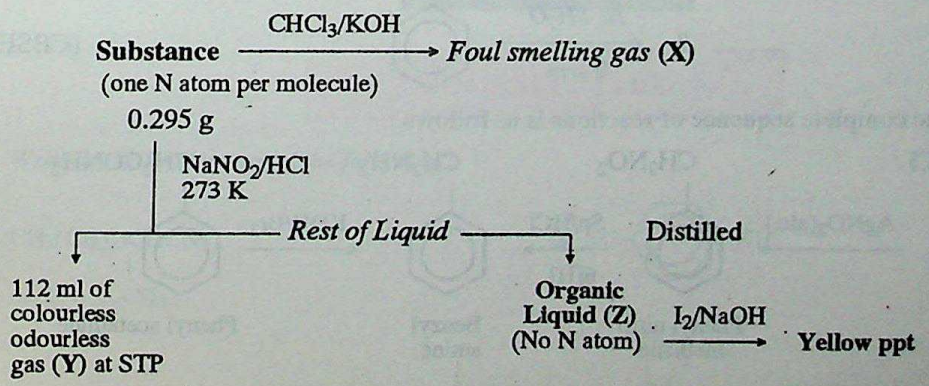
The sequence of reaction can be framed as follows. The starting compound must contain a benzene nucleus and its formula could be $C_6H_5—CH_3$, *i.e.* **toluene.**



Example 9.7. *A basic, volatile nitrogen compound gave foul smelling gas when treated with chloroform and alcoholic potash, 0.295 g of sample of substance, dissolved in HCl and treated with $NaNO_2$ solution gave 112 ml of colourless odourless gas at N.T.P. After evolution of gas was complete the resulting aqueous solution was distilled to give an organic liquid which did not contain N and which on warming with alkali and iodine gave yellow precipitate. Identify original substance. Assume that it contains one N atom per molecule.*

(I.I.T.J.E.E. 1993)

Solution. On arranging the given data in form of tree, we get



(*i*) The organic compound gives foul smelling gas X with $CHCl_3$/KOH. Therefore, it contains primary amino group ($-NH_2$). Let its formula be $R—NH_2$.

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(*ii*) The reaction of R—NH_2 and $NaNO_2$/HCl is described as

$$\underset{(0.295\ g)}{R{-}NH_2} + HONO \xrightarrow{NaNO_2/HCl} \underset{\left(\text{Organic Liquid (Z)}\right)}{R{-}OH} + H_2O + \underset{\left(\text{112 ml of gas Y}\right)}{N_2}$$

(*iii*) Since organic liquid Z (R—OH) gives yellow ppt. of CHI_3, therefore, —OH group must be linked to secondary C. This implies that —NH_2 group in the substance should also be linked to secondary carbon atom.

(*iv*) 112 ml of N_2 at S.T.P. is produced from substance = 0.259 g

22400 ml of N_2 at STP will be produced from $= \dfrac{0.259 \times 22400}{112}$ g = 59 g

∴ Molecular mass of substance = 59 g mol^{-1}

If the formula of R— is C_nH_{2n+1}

Then molecular mass of substance $C_nH_{2n+1}NH_2$ is = $14n + 17$

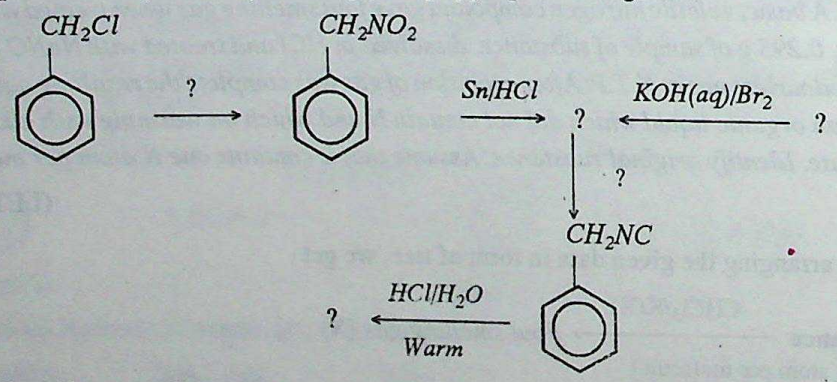
Now $14n + 17 = 59$

$n = 3$

Thus, R— contains 3 carbon atoms.
Hence, the formula of the compound is

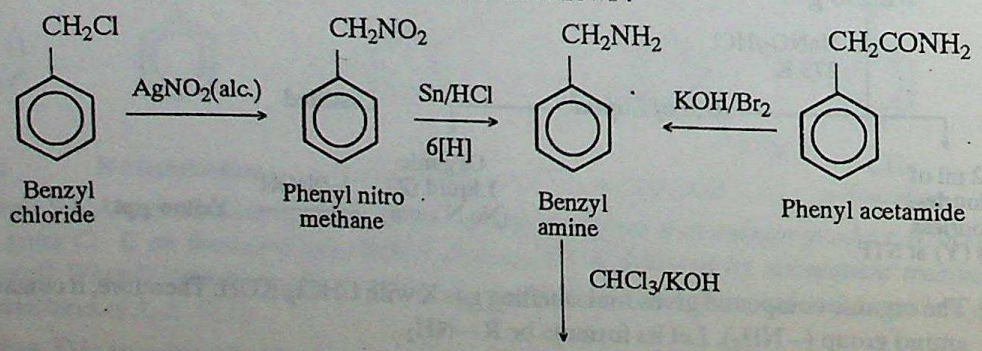
$$CH_3{-}\underset{|}{CH}{-}NH_2.$$

Example 9.8. *Complete the following giving appropriate reagents :*



(CBSE 1995)

Solution. The complete sequence of reactions is as follows :



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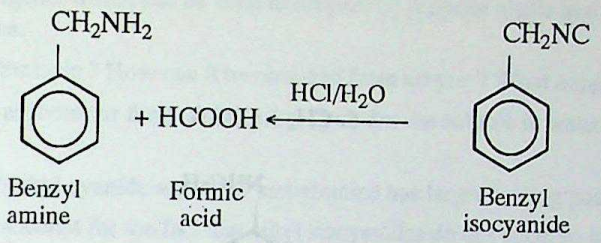
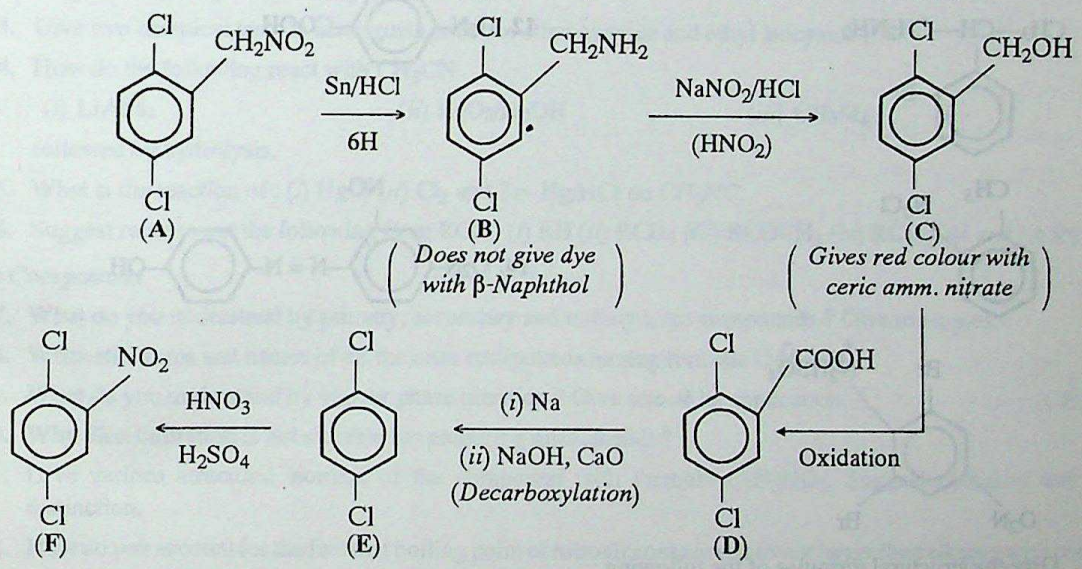


Example 9.9. *An aromatic compound (A) $C_7H_5NO_2Cl$ on reduction with Sn/HCl gives (B), which on reaction with $NaNO_2$/HCl gives (C). The compound (B) does not form dye with β-naphthol. But (C) does give red colour with ceric ammonium nitrate and on oxidation it gives (D) with mol. mass 191. Decarboxylation of (D) gives (E), which gives single mononitro derivative (F) on nitration. Give structures of (A) to (F) with proper reasoning.* (Roorkee 1995)

Solution. The structure of (A) to (F) along with sequence of reactions is as follows :

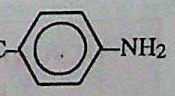


EXERCISES

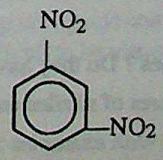
NOMENCLATURE

Write the IUPAC names of the following :

1. $CH_3(CH_2)_3CH(CH_3)CN$

2. 

3. $CH_3CH(NO_2)CH_2CH(NO_2)CH_3$

4. 

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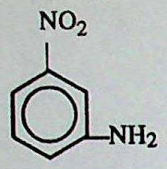
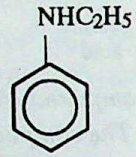
5. 

6. $CH_2 = CHCN$

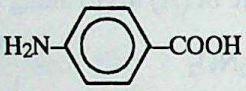
7. $CH_3—CH_2—CH(NO_2)—COOH$

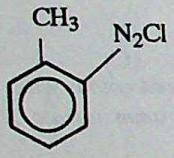
8. 

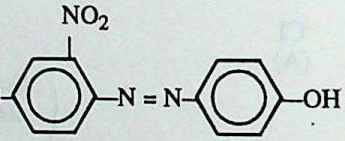
9. $CH_3CH(NO_2)CH_2CH_2NHCH_3$

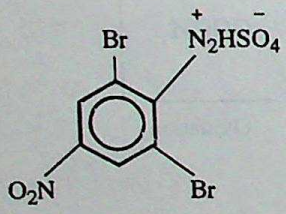
10. $C_6H_5\overset{+}{N}(CH_3)_3\overset{-}{I}$

11. $CH_3—CH(C_6H_4—Br)—CH_2NH_2$

12. 

13. 

14. 

15. 

16. Give the structural formulae of the following :

(*i*) 3-Cyano-1, 5-pentane dinitrile (*ii*) Isobutyronitrile (*iii*) Isopropyl carbylamine

(*iv*) N-Ethylbenzene sulphonamide (*v*) 2-(N-methyl amino) heptane

(*vi*) Ethylidene diamine (*vii*) *o*-Phenylene diamine (*viii*) Diethyl sec. butyl amine

(*ix*) Benzyl aniline (*x*) *p*-Toludine.

17. Name the following compounds according to IUPAC system :

(*i*) $CH_3 . CH = CH . CH_2NH_2$ (*ii*) $CH_2 = CH . CN$. **(*CBSE 1997*)**

DESCRIPTIVE QUESTIONS
(2 or 3 Marks)

Cyanides and Isocyanides

1. What are nitriles and isonitriles ? Do they have any relationship with each other ?
2. Give various isomeric structures of nitriles and isonitriles having molecular formula C_4H_7N.
3. Illustrate the following terms with examples :

(*i*) Electrophile (*ii*) Nucleophile (*iii*) Ambident nucleophile.

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4. Name the reagents which can be used to prepare (*i*) propane nitrile and (*ii*) ethyl carbylamine from ethyl iodide. Give reactions.
5. What is acrylonitrile ? How can it be obtained from ethyne ? What happens when it is hydrolysed ?
6. How do you account for the fact that alkyl cyanides are soluble in water whereas alkyl isocyanides are insoluble in water ?
7. Which out of ethyl cyanide and ethyl carbylamine has larger boiling point and why ?
8. How do you account for the fact that alkyl isocyanides do not undergo basic hydrolysis ?
9. What is Mendius reaction ? Give equation.
10. KCN generally gives cyanides as major product on treatment with alkyl halides, on the other hand, AgCN gives isocyanides as major product why ?
11. Using $SOCl_2$, which chemical compound can be used to prepare benzenenitrile.
12. An alkyl cyanide with five carbon atoms and containing only primary H atoms is subjected to hydrolysis. Name the product giving chemical equation.
13. Give two chemical tests to distinguish between ethyl cyanide and ethyl isocyanide.
14. How do the following react with CH_3CN

    (*i*) $LiAlH_4$ (*ii*) $H_2O_2/NaOH$ (*iii*) CH_3MgI

    followed by hydrolysis.
15. What is the reaction of : (*i*) HgO, (*ii*) Cl_2 and Zn- Hg/HCl on CH_3NC.
16. Suggest route to get the following from RCN : (*i*) RH (*ii*) RCH_3 (*iii*) $RCOCH_3$ (*iv*) RCH_2OH and (*v*) $RCOOCH_3$.

Nitro Compounds

17. What do you understand by primary, secondary and tertiary nitro compounds ? Give examples.
18. Write structures and names of all the nitro compounds having formula $C_7H_7NO_2$.
19. What do you understand by vapour phase nitration ? Give one of its application. *(CBSE 1992)*
20. Why direct nitration is not suitable for preparing nitroalkanes ?
21. Give various structural isomers of the compound with formula $C_2H_5NO_2$. Suggest chemical test for their distinction.
22. How do you account for the fact that boiling point of nitroalkanes are relatively larger than alkanes with comparable molecular masses.
23. Alcoholic $AgNO_2$ mainly forms nitroalkane when treated with alkyl halides but KNO_2 mainly gives alkyl nitrite.
24. Out of CH_3NO_2 and CH_3ONO which one has higher boiling point ?
25. Name the attacking electrophile during nitration of benzene. Give its structure and shape.
26. Arrange, benzene, toluene and nitrobenzene in order of decreasing reactivity towards electrophilic substitution.
27. Give various primary, secondary and tertiary nitro compounds with formula $C_4H_9NO_2$. How do they differ towards (*i*) Hydrolysis (*ii*) Action with HNO_2.
28. Which reagent can be employed to convert 2-methyl propanenitrile to isobutyl amine. Give equation.
29. Give reduction products of nitrobenzene under following conditions :

    (*i*) Sodium arsenite/NaOH (*ii*) Zn/NaOH

    (*iii*) $LiAlH_4$ (*iv*) Zn/NH_4Cl and Sn/HCl.
30. What is Baker-Mulliken's test ? Which functional group of organic compounds is tested by the above test ?
31. In contrast to arenes, the aliphatic hydrocarbons are difficult to be nitrated *(Delhi Board 1992)*
32. Give the mechanism of nitration of benzene. *(Panjab Board 1994)*
33. For nitromethane molecule give the following :

    (*i*) Structures showing resonance (*ii*) Structures showing tautomerism *(I.I.T. 1986)*

    (*iii*) Reaction with Cl_2 in the presence of alkali.

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34. Why does nitrobenzene gives *m*-chloronitrobenze instead of ortho or para product on chlorination ?

35. Give IUPAC name of reactant and also its product with H_2/Pt. The reactant is $CH_3—\underset{\underset{CH_2—NO_2}{|}}{CH}—CH = CH—NO_2$.

36. Name two important nitrocompounds which are widely used as explosives.

37. Which reagent can be used for the selective reduction of *m*-dinitrobenzene ?

Amines

38. Give the method for the preparation of pure primary amines from alkyl halides.

39. How would you separate chemically, a mixture of nitrobenzene and aniline ?

40. Why is it difficult to prepare pure primary amines by ammonolysis of alkyl halides ?

[*Pb. Board 1992 ; A.I. CBSE (1) 1992*]

41. Give the common and IUPAC name of the structure of amine with five carbon atoms and having only primary H atoms. How many other structures of primary amine of same formula are possible ? How many of these are optically active ?

42. Give the names of two possible amines which can be obtained from benzamide. How do they differ ?

43. Account for the fact that $R\ddot{N}H_2$ is more basic than NH_3.

44. Aniline is less basic than ammonia as well as $C_2H_5NH_2$.

45. What is the effect of substitution of electron releasing and electron withdrawing groups on the basic strength of aniline ?

46. Arrange the following in the increasing order of their basic strength ?

(*i*) Ethyl amine (*ii*) Diethyl amine (*iii*) Aniline.
(*iv*) Ethanamide (*v*) Ammonia.

47. Out of ethyl amine and ethyl alcohol which has higher boiling point ? (*Delhi Board 1992*)

48. What is the increasing order of basic strength among ethyl amine, diethyl amine and triethyl amine in
(*a*) aqueous medium (*b*) in gas phase. (*Pb. Board 1992*)

49. Which of the following is a better nucleophile, aniline or anilinium ion ? Justify your answers.

50. Account for the fact that electrophilic substitution in aniline takes place far more rapidly than in benzene.

51. Aniline is weaker base than cyclohexyl amine. Why ?

52. Suggest brief explanation of each of the following :

(*i*) Lower aliphatic amines are soluble in water.
(*ii*) Silver chloride dissolves in aqueous solution of methylamine.
(*iii*) Copper (II) sulphate solution gives deep blue colour on shaking with ethylamine.

53. Starting from aniline how would you get
(*a*) *p*-bromobenzene (*b*) benzene diazonium chloride
(*c*) acetanilide (*d*) benzanilide.

54. How do the following pair of species react ? Give proper conditions and chemical equations.

(*i*) Ethyl amine and nitrous acid (*ii*) Aniline and nitrous acid
(*iii*) Ethyl amine and ethyl magnesium bromide. (*Har. Board 1987*)

55. Illustrate each of the following with one example :

(*i*) Ammonolysis (*ii*) Acylation
(*iii*) Zwitter ion (*iv*) Hinsberg test. (*Delhi Board 1992*)

56. Discuss each of the following in brief :

(*i*) Hoffmann bromamide reaction (*CBSE 1992 ; PSMB Board 1992 ; H.P. Board 1993*)

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(*ii*) Carbylamine reaction (*H.P. Board 1992, 93*)

(*iii*) Gabriel phthalimide reaction

(*iv*) Coupling reaction (*Pb. Board 1993, 95*)

(*v*) Diazotisation reaction. (*H.P. Board 1995*)

57. Explain giving equation the reaction of nitrous acid with secondary amine. (*Har. Board 1995*)

58. Mention the chief use of quaternary ammonium salt derived from long chain amines. (*CBSE 1994*)

59. Give the structures of various amines with formula C_3H_9N. Answer the following :

(*i*) How do they react with HNO_2 ?

(*ii*) Which one reacts with benzene sulphonyl chloride to give a solid insoluble in alkali ? (*I.I.T. 1993*)

(*iii*) Which one has a least boiling point ?

(*iv*) Which one is capable of giving carbylamine test ?

(*v*) Which one is least basic in aqueous medium ?

60. During nitration or mono bromination of aniline why is it necessary to carry out acylation first ?

62. How can benzene diazonium chloride be prepared from aniline ? How can it be converted into

(*i*) Benzene (*ii*) Nitrobenzene

(*iii*) Cyanobenzene (*iv*) Fluorobenzene.

63. How does benzene diazonium chloride react with (*a*) KI on warming (*b*) Alkaline phenol in ice cold solution. (*Pb. Board 1993*)

64. How is aniline distinguished from N-methylaniline ? Give reaction. (*Delhi Board 1994*)

65. Explain giving reasons :

(*i*) Arylamines are weaker bases than alkyl amines.

(*ii*) Silver chloride dissolves in methylamine solution. (*CBSE 1997*)

66. Suggest chemical test to distinguish between primary secondary and tertiary amines.

67. Suggest a convenient scheme for separating, aniline, N-methyl aniline, phenol and toluene other than distillation. (*I.I.T. 1988*)

Miscellaneous Questions

68. An organic compound **A** on boiling with alkali gives ammonia and sodium salt of acid **B**, which is monobasic acid that can be obtained from 1-propanol ? When reduced A forms **C**, which on subsequent treatment with nitrous acid gave **D**. Give the sequence and structures of A, B, C, D.

69. A simple secondary amine has vapour density 36. On heating amine with excess of CH_3I for a long time a quaternary salt with molecular mass 229 is formed. Predict the structural formula of amine. Also suggest the structure of its metamer.

70. An organic compound **A** contains 69.42% C, 5.78% hydrogen and 11.57% N and has vapour density 60.5. **A** gives ammonia on boiling with caustic potash. On heating with P_2O_5 **A** gives **B** containing 81.55% C, 4.85% hydrogen and 13.95% N. On reduction with sodium/alcohol **B** forms a base which reacts with HNO_2 giving off nitrogen and yielding alcohol **C**. The alcohol can be oxidised to benzoic acid. Give the structures of A, B, C. (*Roorkee 1982*)

71. An organic compound **A** gives a primary amine **B** on reduction. **B** reacts with nitrous acid to form **C**, an alcohol with two carbon atoms. **B** also gives intolerable smell when warmed with chloroform and KOH and also forms compound **D**. **D** gives another amine **E** on reduction. Suggest the structures of A, B, C, D, E giving sequence of reactions.

72. A compound **X** with molecular formula C_3H_7NO and hydrolysis gave amine **Y** and a carboxylic acid **Z**. Amine **Y** reacts with benzene sulphonyl chloride and gives a product which is insoluble in sodium hydroxide. Acid **Z** on the other hand gives a silver mirror with Tollen's reagent. Suggest the structures of **X**, **Y** and **Z**.

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73. An organic compound **X** with formula $C_6H_4N_2O_4$ is subjected to reduction using Na_2S. The reduction product **Y**, $C_6H_6N_2O_2$ was diazotised with HNO_2 at 278 K. The diazotised product on treatment with CuBr/HBr gave **Z**. **Z** on reaction with sodium metal in dry ether gave **W**. Prolonged refluxing of benzene with conc. HNO_3 and conc. H_2SO_4 at 513 K also gave **X**. Identify **X, Y, Z, W** giving sequence of reactions.

74. Certain organic compound **A** containing C, H, N, O on hydrolysis gives alcohol **B** with molecular mass 46 and an acid. The same alcohol can also be produced along with NH_3 gas by reduction of compound **A**. **A** can also be produced from ethyliodide by treating with reagent **C**. What is A, B, C ?

75. An organic compound A with formula $C_9H_{13}N$ dissolves in dilute HCl and gives off N_2 with HNO_2 giving an optically active aromatic alcohol B. The alcohol B on oxidation gives dicarboxylic acid, which on heating forms anhydride ? What are A and B ?

76. A mixture of two aromatic compounds (A) and (B) was separated by dissolving in $CHCl_3$ followed by extraction with KOH solution. The organic layer containing A when heated with alcoholic solution of KOH produces C (C_7H_5N) associated with unpleasant odour. The alkaline aqueous layer on the other hand, when heated with chloroform followed by acidification gave a mixture of two isomeric compounds D and E of formula $C_7H_6O_2$. Identify A to E. ***(I.I.T. 1990)***

COMPLETING THE EQUATIONS
(1 Mark)

Complete the following giving chemical equations :

1. $CH_3NC + 2H_2O \xrightarrow{H^+} .....$

2. $C_2H_5CN + 2H_2O \xrightarrow{HCl} .....$

3. $C_2H_5CH_2CN \xrightarrow{Na/C_2H_5OH} .....$

4. $CH_3CH_2NC \xrightarrow{LiAlH_4} .....$

5. $C_2H_5NC \xrightarrow{HgO} .....$

6. $R—NC \xrightarrow{H_2/Pt} .....$ ***(Delhi Board 1993)***

7. $C_6H_5CONH_2 \xrightarrow{SOCl_2} .....$ ***(CBSE 1993)***

8. $C_2H_5NO_2 \xrightarrow{H_2O/H^+} .....$

9. $C_6H_5NO_2 \xrightarrow{LiAlH_4} .....$

10. $(CH_3)_2CHNO_2 \xrightarrow{HCl} .....$

11. $CH_3CH_2NO_2 \xrightarrow[NaOH]{Br_2} .....$

12. $CH_3CH_2NH_2 \xrightarrow[Boiling]{HCl} .....$ ***(Har. Board 1988)***

13. $CH_3NH_2 \xrightarrow{HNO_2} .....$ ***(Delhi Board 1986 ; BIT Ranchi 1992)***

14. $C_2H_5NH_2 \longrightarrow .....$

15. $C_6H_5NH_2 \xrightarrow[H_2SO_4]{Conc.} .....$ ***[A.I. CBSE (O) 1989]***

16. $C_6H_5NH_2 \xrightarrow[CH_3I]{Excess} .....$

17. $ArN_2Cl + H_3PO_2 + H_2O \longrightarrow .....$ ***(CBSE 1993)***

18. $C_6H_5N_2Cl \xrightarrow[KCN]{CuCN} .....$

19. $C_2H_5NH_2 \xrightarrow{AgCl} .....$ ***(CBSE 1989)***

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20. $RNH_2 \xrightarrow{CHCl_3/KOH}$ ..... *(Delhi Board 1991)*

21. $CH_3CONH_2 + Br_2 + NaOH \longrightarrow$ ..... *(Har. Board 1992)*

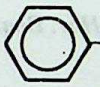
22. $C_6H_5NH_2 + Br_2 \longrightarrow$ ..... *(CBSE 1985 ; H.P. Board 1990)*

23. $C_6H_5NH_2 \xrightarrow{Na_2Cr_2O_7/H_2SO_4}$ ..... *(H.P. Board 1991)*

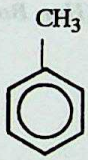
Identify A, B, C, D, etc. in each of the following questions giving chemical equation :

24. $C_6H_5NO_2 \xrightarrow{Fe/Br_2} (A) \xrightarrow{H_2/Pt} (B) \xrightarrow{NaNO_2/HCl} (C)$ *(Roorkee Ent. 1987)*

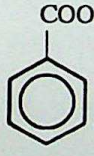
25. $C_6H_5COOH \xrightarrow{(A)} C_6H_5COCl \xrightarrow{NH_3} (B) \xrightarrow{(C)} C_6H_5CN.$ *(Roorkee Ent. 1988)*

26.  $-CONH_2 \xrightarrow{P_2O_5} (A) \xrightarrow[\Delta]{H_2O/H^+} (B).$ *(I.I.T.J.E.E. 1992)*

27. $C_6H_5CN \xrightarrow{H_2/Ni} A \xrightarrow{(i)\ NaNO_2/HCl} \xrightarrow[H_2O]{(ii)\ Warm} B$

28. 

$\xrightarrow[H_2SO_4\ (Major)]{HNO_3} A \xrightarrow{Fe/HCl} B \xrightarrow[HCl]{NaNO_2} C \xrightarrow[(ii)\ H_3O^+]{(i)\ CuCN} D$

29. 

$\xrightarrow[Heat]{NH_3} A \xrightarrow{Br_2/KOH} B \xrightarrow[(ii)\ Steam]{(i)\ NaNO_2/HCl} C$

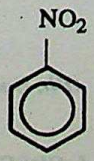
30. $CH_2 = CH_2 \xrightarrow{HI} A \xrightarrow[C_2H_5OH]{AgCN} B \xrightarrow{S_8} C$

31. $C_6H_6 \xrightarrow{A} C_6H_5NO_2 \xrightarrow[NaOH]{Glucose} B$

32. $(CH_3)_2CHBr \xrightarrow{A} (CH_3)_2CHNO_2 \xrightarrow[HCl]{Boiling} B$

33. $C_6H_5NH_2 \xrightarrow{CH_3I} A \xrightarrow{CH_3I} B \xrightarrow{HNO_2} C$

34. $CH_3(CH_2)_2CONH_2 \xrightarrow[Heat]{P_2O_5} A \xrightarrow{H_2/Pt} B \xrightarrow{NaNO_2/HCl} C$

35. 

$\xrightarrow{Sn/HCl} A \xrightarrow{Br_2\ (Excess)} C \xrightarrow[5°C]{NaNO_2\ (HCl)} D \xrightarrow[H_2O]{H_3PO_2} E.$ *(Delhi Board 1995)*

$A \xrightarrow{KOH/Br_2} B$

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WHAT HAPPENS WHEN
(1 Mark)

State giving equations as to what happens when

1. Benzyl cyanide is reduced with tin (II) chloride and hydrochloric acid in ethereal solution at 290 K following by hydrolysis.
2. Methyl isocyanide is treated with Cl_2.
3. Phenyl acetonitrile is boiled with dilute H_2SO_4.
4. Ethyl isocyanide reacts with sulphur. ***(Har. Board 1992)***
5. *n*-Propyliodide is treated with alcoholic solution of silver nitrite.
6. 1, 3-Dinitrobenzene is reduced with sodium polysulphide.
7. Toluene is treated with a mixture of conc. HNO_3 and conc. H_2SO_4.
8. Nitrobenzene is reduced with zinc dust and ammonium chloride. ***(Har. Board 1995)***
9. Nitromethane is treated with excess of Cl_2 in NaOH.
10. Nitroethane is boiled with dilute HCl.
11. Acetaldoxime is reduced with lithium aluminium hydride.
12. Benzamide is allowed to react with Br_2 and alcoholic KOH. ***(Har. Board 1992)***
13. Ethyl amine reacts with silver chloride. ***(Har. Board 1992)***
14. Propanal is subjected to reductive amination.
15. Ethyl amine is slowly oxidised in air.
16. Benzal aniline is reduced by H_2/Raney Ni.
17. N, N-Dimethyl aniline is allowed to react with nitrous acid.

CONVERSIONS

Bring about the following organic conversions :

1. Nitrobenzene to benzene nitrile.
2. Aniline to *p*-hydroxy azobenzene. ***(H.P. Board 1990)***
3. *n*-Propyl chloride to *n*-propyl amine. ***(Pb. Board 1989)***
4. Benzene to 4-bromonitrobenzene.
5. Benzene to 3-nitroaniline.
6. Aniline to *p*-nitroaniline.
7. Methyl amine to ethyl amine.
8. Ethanamine to methanamine. ***(Pb. Board 1992)***
9. Toluene to *m*-chlorotoluene.
10. Benzene to *m*-nitrochlorobenzene.
11. Aniline to *p*-bromoacetanilide.
12. Ethanamine to ethyl isocyanide.
13. Ethylamine to ethyl ethanoate. ***(Pb. Board 1993)***
14. Aniline to phenyl isocyanide.
15. Aniline to benzonitrile. ***[A.I. CBSE (2) 1992]***

[A.I. CBSE (3) 1992]

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16. Aniline to *p*-sulphanilic acid. [*A.I. CBSE (4) 1992 ; Pb. Board 1993*]
17. CH_3NC to $(CH_3)_2NH$. (*Pb. Board 1993*)
18. Aniline to phenyl cyanate. (*Pb. Board 1993*)
19. Aniline to fluorobenzene. (*Delhi Board 1993*)
20. Aniline to phenyl thiocyanate. (*Pb. Board 1994*)
21. Benzene diazonium chloride to phenol. (*Pb. Board 1995*)
22. Benzene to *m*-bromophenol.
23. Aniline to benzoic acid.
24. *p*-Chloroaniline to *p*-chlorobenzylamine.
25. Hexane nitrile to 1-aminopentane.
26. Benzene to 1, 3, 5-tribromobenzene.

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

1. The reduction product of alkyl isocyanides is
   (*a*) 1° Amine (*b*) 2° Amine (*c*) 3° Amine (*d*) quaternary salt.
2. The formula of acrylonitrile is
   (*a*) $CH_3CH = C—CN$ (*b*) $CH_2 = CHCN$ (*c*) $NC—CH = CH—CN$ (*d*) $HC \equiv C—CN$.
3. The nitration of benzene is
   (*a*) electrophilic substitution (*b*) electrophilic addition
   (*c*) nucleophilic substitution (*d*) nucleophilic addition.
4. Potassium phthalimide on treating with alkyl halide and followed by hydrolysis gives a primary amine. The reaction is called
   (*a*) Mendius reaction (*b*) Gabriel synthesis
   (*c*) Hofmann's degradation (*d*) Cannizaro's reaction.
5. Lower amines are soluble in water due to
   (*a*) low molecular mass (*b*) formation of complexes
   (*c*) formation of hydrogen bonds with water (*d*) affinity with water.
6. Which one of the following amines gives an alcohol with nitrous acid ?
   (*a*) CH_3NH_2 (*b*) $(CH_3)_2NH$ (*c*) $(CH_3)_3N$ (*d*) $C_6H_5NH_2$.
7. Which one of the following amines does not react with acetyl chloride ?
   (*a*) $C_2H_5NH_2$ (*b*) $(CH_3)_2NH$ (*c*) $(CH_3)_3N$ (*d*) CH_3NH_2.
8. Which one of the following amines reacts with chloroform and alkali to give an isocyanide ?
   (*a*) $C_2H_5NH_2$ (*b*) $(CH_3)_2NH$ (*c*) $(C_2H_5)_3N$ (*d*) $(CH_3)_2NH$.
9. Reaction of $R—\overset{\overset{O}{\|}}{C}—NH_2$ with a mixture of Br_2 and KOH gives RNH_2 as main product. The intermediate involved in the reaction are
   (*a*) $R—\overset{\overset{O}{\|}}{C}—NHBr$ (*b*) $R—N = C = O$
   (*c*) $R—NH—Br$ (*d*) $H—CO—NBr_2$. (*I.I.T.J.E.E. 1992*)
10. On treatment with a mixture of sodium nitrite and dil. HCl at 278 K, aniline gives
    (*a*) phenol (*b*) benzene diazonium chloride
    (*c*) phenyl isocyanide (*d*) none of these.
11. Activation of benzene ring in aniline can be decreased by treating with
    (*a*) dil. HCl (*b*) ethyl alcohol
    (*c*) acetic acid (*d*) acetyl chloride.
12. Which of the following on dehydration with P_2O_5 will give ethanenitrile ?
    (*a*) Ethanol (*b*) Ethanamide
    (*c*) Propanamide (*d*) Isobutyramide.

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13. Which of the following is ambident nucleophile ?

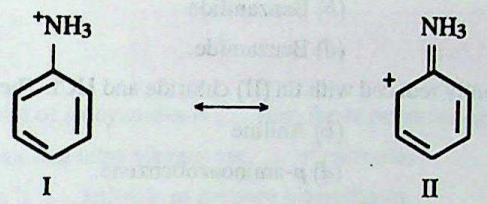
(*a*) : $\bar{O}H$ (*b*) $\bar{C}N$ (*c*) : $\bar{S}H$ (*d*) all the above.

14. Basic hydrolysis of alkyl cyanide produces

(*a*) Carboxylic acid (*b*) Salt of ammonia

(*c*) Salt of carboxylic acid (*d*) $NaNH_2$.

15.



Which of the statement about the two structures is correct ?

(*a*) II is not an acceptable cannonical structure because carbonium ions are less stable than ammonium ions.

(*b*) II is not acceptable structure because it is non-aromatic.

(*c*) II is not acceptable cannonical structure because N has 10 valence electrons.

(*d*) II is an acceptable cannonical structure. ***(I.I.T. J.E.E. 1993)***

16. Which of the following does not react with Hinsberg reagent ?

(*a*) Ethylamine (*b*) $(CH_3)_2NH$

(*c*) $(CH_3)_3N$ (*d*) Propan-2-amine.

17. $C_2H_5NH_2 \xrightarrow{NaNO_2/HCl} X \xrightarrow{P/Br_2} Y \xrightarrow[\text{(excess)}]{NH_3} Z$

In the above sequence, Z is

(*a*) Cyanoethane (*b*) Ethanamide

(*c*) Methanamine (*d*) Ethanamine.

18. Oxidation of aniline with $K_2Cr_2O_7/H_2SO_4$ gives

(*a*) phenylhydroxyl amine (*b*) *p*-benzoquinone

(*c*) nitrosobenzene (*d*) nitrobenzene.

19. Which of the following amines can exhibit enantiomerism ?

(*a*) Benzenamine (*b*) 2-Butanamine

(*c*) 2-Propanamine (*d*) 2-Methyl-2-propanamine.

20. Which of the following ; when heated with a mixture of ethanamine and alcoholic potash gives ethyl isocyanide ?

(*a*) 2-chloropropane (*b*) 2, 2-dichloropropane

(*c*) trichloromethane (*d*) tetrachloromethane.

21. Which of the following pairs of species will yield carbylamine ?

(*a*) CH_3CH_2Br and KCN (*b*) CH_3CH_2Br and NH_3 (excess)

(*c*) CH_3CH_2Br and AgCN (*d*) $CH_3CH_2NH_2$ and HCHO.

22. The main product of reaction of alcoholic silver nitrite and ethyl bromide is

(*a*) ethane (*b*) ethyl nitrite

(*c*) ethyl isocyanide (*d*) nitroethane. ***(I.I.T. 1991)***

23. Which of the compound is most reactive towards ring nitration ?

(*a*) Toluene (*b*) Benzene

(*c*) Benzoic acid (*d*) Nitrobenzene. ***(I.I.T. 1985)***

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24. $C_6H_5\overset{+}{N_2}\overset{-}{Cl} + CuCN \longrightarrow C_6H_5CN + N_2 + CuCl$

The above chemical reaction is associated with which of the following name

(*a*) Balz Schiemen (*b*) Gattermann

(*c*) Shimonini (*d*) Sandmeyer.

25. The reaction of aniline with benzoyl chloride gives

(*a*) Benzoin (*b*) Benzanilide

(*c*) Benzalaniline (*d*) Benzamide.

26. Aniline was diazotised and was subsequently reduced with tin (II) chloride and HCl. The product formed is

(*a*) Phenylhydrazine (*b*) Aniline

(*c*) Phenyl aniline (*d*) *p*-aminoazobenzene.

27. Which of the following will not give primary amine ?

(*a*) Dehydration of amide (*b*) Acidic hydrolysis of alkyl isocyanides

(*c*) Reduction of amides (*d*) Reduction of alkyl cyanides.

28. The reagents used in Hoffman's Mustred oil reaction are

(*a*) Mustred oil and 1° amine (*b*) CS_2 and aniline in $HgCl_2$

(*c*) Nitrobenzene and CS_2 (*d*) S and RNC.

29. Which of the following cannot couple with benzene diazonium chloride ?

(*a*) Aniline (*b*) Phenol

(*c*) β-Naphthol (*d*) Benzyl alcohol.

30. The hybrid state of N in R_2NH is

(*a*) sp^3 (*b*) sp^2

(*c*) sp (*d*) dsp^2.

ASSERTION-REASON TYPE QUESTIONS

Each of the Questions 31 to 35 given below consists of two statements—Assertion and Reason. Select (tick) the correct choice (a), (b), (c) or (d) corresponding to each question as follows :

(*a*) If both assertion and reason are true statements and the reason is a correct explanation of the assertion.

(*b*) If both assertion and reason are true statements and the reason is not a correct explanation of the assertion.

(*c*) If the assertion is true but the reason is a false statement.

(*d*) If both assertion and reason are false statements.

31. ***Assertion.*** At the isoelectric point of an amino acid, it does not migrate under the influence of an electric field.

Reason. An amino acid at the isoelectric point exists as a Zwittex ion.

(*a*) (*b*) (*c*) (*d*).

32. ***Assertion.*** Aniline is stronger base than ammonia.

Reason. In aniline electron density increases at nitrogen due to mesomeric effect.

(*a*) (*b*) (*c*) (*d*).

33. ***Assertion.*** The main product of reaction of alcoholic silver nitrite with ethyl bromide is nitroethane.

Reason. Silver nitrite is predominantly covalent compound.

(*a*) (*b*) (*c*) (*d*).

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34. ***Assertion.*** Ammonolysis of alkyl halides is not a suitable method for the preparation of pure primary amines.
Reason. Ammonolysis of alkyl halides yields mainly secondary amines.
(*a*) (*b*) (*c*) (*d*).

35. ***Assertion.*** Acylation of aniline increases the reactivity of benzene ring (as compound with that in aniline).
Reason. Acylation of aniline results in increase in electron density at the benzene ring.
(*a*) (*b*) (*c*) (*d*).

FILL IN THE BLANKS

1. The boiling point of isocyanides is ..... than the corresponding isomeric cyanides.
2. The alkyl nitrites and nitro alkanes are ..... of each other.
3. Direct nitration is ..... suitable to get pure nitroalkanes.
4. Alkyl nitrite can be considered to be an ..... of alcohol and nitrous acid.
5. Aniline is ..... basic than $\ddot{N}H_3$ whereas ethylamine is ..... basic than $\ddot{N}H_3$.
6. Carbylamine reaction is a test for .....
7. N, N-Dimethyl aniline on treatment with HNO_2 gives .....
8. Schotten-Baumann reaction involves reaction between .....
9. Sulphanilic acid exists as ..... structure.
10. $C_6H_5OH + C_5H_5\overset{+}{N_2}\overset{-}{Cl} \xrightarrow{pH\ 9—10}$ .....
11. Stephan's reduction converts alkyl cyanide into .....
12. Reaction of methyl isocyanides with HgO produces .....
13. Benzene diazonium chloride reacts with ..... to give benzene.
14. *p*-benzoquinone can be obtained from aniline by .....
15. Electrolytic reduction of nitrobenzene in strongly acidic medium produces .....

TRUE/FALSE STATEMENTS

1. Aniline is a stronger base than ammonia. ***(B.I.T.S. Ranchi 1992)***
2. In Hoffmann bromamide reaction amide is converted into amine with one carbon atoms less than the parent amide.
3. Amide can also produce nitrile by treatment with NaOH.
4. Carbylamine reaction is shown by 1° as well as 2° amines.
5. Ethyl amine does not have any reaction with $CuSO_4$ solution.
6. Reaction of $AgNO_2$ with ethyl iodide not only produces nitroethane but also ethylnitrite.
7. Both cyanides and nitrites are ambident nucleophiles.
8. Reduction of nitrobenzene with H_2 in presence of platinum gives nitrosobenzene.
9. Ethyl amine forms salts with alkalies.
10. Gabriel phthalimide synthesis cannot yield 2° amines.
11. Tertiary amines give alkanes with alkyl magnesium halide.
12. Alkyl diazonium salts are very unstable.
13. Benzylamine is stronger base than aniline.
14. Nitrobenzene is less reactive towards nitration in comparison to benzene.
15. Pseudonitrol is formed by the reaction of primary nitroalkane and nitrous acid.

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MATCHING THE ITEMS

Match the items of column A, B and C

A	B	C
1. Nitroethane	1. Benzonitrile	1. Sulphonation of aniline
2. Aniline	2. Stronger base than ethyl amine	2. Caused Bhopal tragedy in 1984
3. C_6H_5CN	3. Reduction product of $C_6H_5NO_2$	3. Gives nitrolic acid with HNO_2
4. Diethylamine	4. Zwitter ion	4. Cannot be used to prepare 2° and 3° amines
5. Phenylhydroxylamine	5. $C_2H_5I + AgNO_2$	5. Gives benzoic acid
6. *p*-amino benzene sulphonic acid	6. MIC	6. Benzylamine
7. Phthalimide	7. $C_6H_5CH_2NH_2$	7. Gives orange dye with diazonium chloride
8. $CH_3—N = C = O$	8. C is in *sp*-hybrid state	8. Does not react with $CHCl_3$/KOH
9. HCN	9. Gabriel synthesis	9. Gives silver, mirror with Tollen's reagent
10. Aryl alkyl amine	10. 1° amine	10. Prussic acid

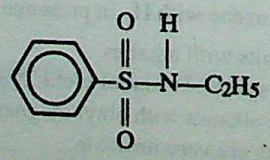
HINTS AND ANSWERS

NOMENCLATURE

1. 2-Methylpentanenitrile
2. 4-Aminobenzenenitrile
3. 2, 4-Dinitropentane
4. 1, 3-Dinitrobenzene
5. 3-Nitrobenzenamine
6. Prop-2-enenitrile
7. 2-Nitrobutanoic acid
8. N-Ethylbenzenamine
9. 3-Nitro-1-N-methylbutanamine
10. Trimethyl phenyl ammonium iodide
11. 2-(*o*-Bromophenyl)-1-propanamine
12. 4-Aminobenzoic acid
13. 2-Toluenediazonium chloride
14. 4-Hydroxy, (2, 4-dinitro) azobenzene
15. 2, 6-Dibromo-4-nitrobenzene diazonium hydrogen sulphate
16. (*i*) $CH_2(CN)—CH(CN)—CH_2(CN)$

(*ii*) $CH_3CH(CH_3)—CN$

(*iii*) $CH_3CH(CH_3)—N \equiv C$

(*iv*) 

(*v*) $CH_3CH(NH)CH_2CH_2CH_2CH_2CH_3$

(*vi*) $CH_3—CH(NH_2)—NH_2$

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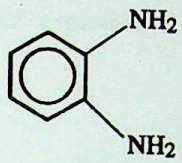
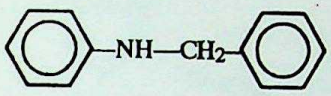
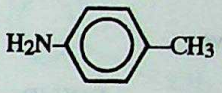
(*vii*) 

(*viii*) $C_2H_5-N(C_2H_5)-CH(CH_3)-CH_2CH_3$

(*ix*) 

(*x*) 

DESCRIPTIVE QUESTIONS

2. $CH_3CH_2CH_2CN$ Butane nitrile; $CH_3CH(CH_3)-CN$ 2-Methyl propane nitrile; $CH_3CH_2CH_2NC$ *n*-Propyl carbylamine; $CH_3CH(CH_3)-NC$ Isopropyl carbylamine

5. $CH_2 = CHCN$; $CH \equiv CH + HCN \xrightarrow{Ba(CN_2)} CH_2 = CHCN$

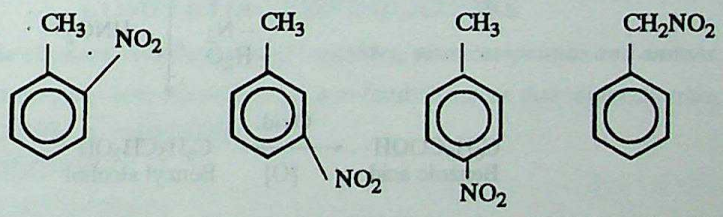
Hydrolysis will produce acrylic acid.

8. Refer section 9.8.

10. Refer section 9.6.

11. $C_6H_5CONH_2$

12. $CH_3-C(CH_3)_2-CN \longrightarrow CH_3-C(CH_3)_2-COOH$

18. The structures are 

21. $CH_3CH_2-\overset{\overset{O}{\uparrow}}{N} = O$ and $CH_3CH_2-ON = O$

26. $C_6H_5-CH_3 > C_6H_5 > C_6H_5NO_2$

34. NO_2 group is *m*-directing. NO_2 group deactivates the benzene ring making *o* and *p* positions deficient in electron density. The meta position is relatively richer in electron density and readily undergoes electrophilic attack.

37. Na_2S_x or $(NH_4)_2 S_x$

41. $CH_3-C(CH_3)_2-CH_2NH_2$ (Neopentyl amine)

The other structures of 1° amine are as

(A) $CH_3CH_2CH_2CH_2CH_2NH_2$, (B) $CH_3CH_2CH(CH_3)-NH_2$, (C) $CH_3CH_2CH(NH_2)CH_2CH_3$,

(D) $CH_3CH_2CH(CH_3)CH_2NH_2$, (E) $CH_3CH(CH_3)CH_2CH_2NH_2$, (F) $CH_3CH(CH_3)-CH(CH_3)-NH_2$

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(G) $CH_3-C(NH_2)(CH_3)-CH_2CH_3$

B, D, F are optically active

42. $C_6H_5CH_2NH_2 \xleftarrow{H_2/Pt} C_6H_5CONH_2 \xrightarrow{KOH/Br_2} C_6H_5NH_2$

Benzylamine Benzamide Aniline

46. Ethanamide < Aniline < $\ddot{N}H_3$ < ethylamine < diethylamine

Acylation decreases the reactivity of the ring and it protects the $—NH_2$ group from oxidation.

MISCELLANEOUS QUESTIONS

68. **A** is Ethyl cyanide ; **B** is Propionic acid ; **C** is *n*-Propylamine ; **D** is *n*-propyl alcohol.

69. The amine is $(C_2H_5)_2NH$ and its metamer is $CH_3NHCH_2CH_2CH_3$ *i.e.*, methyl propyl amine.

70. **A** is $C_6H_5CONH_2$; **B** is C_6H_5CN ; **C** is $C_6H_5CH_2OH$

The sequence of reactions is

$$\underset{\text{Benzamide}}{C_6H_5CONH_2} \xrightarrow[-H_2O]{P_2O_5} \underset{\text{Benzonitrile}}{C_6H_5CN} \xrightarrow{\text{Red.}} \underset{\text{Benzylamine}}{C_6H_5CH_2NH_2}$$

$$\downarrow \; -N_2, -H_2O \; HNO_2$$

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} \xleftarrow[[O]]{\text{Oxid.}} \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

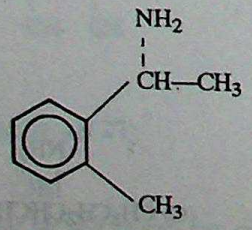
71. **A** is $C_2H_5NO_2$; **B** is $C_2H_5NH_2$; **C** is C_2H_5OH ; **D** is C_2H_5NC ; **E** is $C_2H_5NHCH_3$

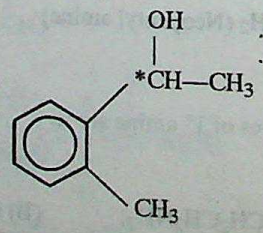
72. **X** is $HCON(CH_3)_2$; **Y** is $(CH_3)_2NH$ and **Z** is HCOOH

73. **X** is *m*-Dinitrobenzene ; **Y** is 3-Nitroaniline, **Z** is *m*-Chloronitrobenzene ; **Z** is 3, 3′ Dinitrobiphenyl

74. **A** is $C_2H_5ON = O$; **B** is C_2H_5OH ; **C** is KNO_2 sequence of reactions

$$\underset{(B)}{C_2H_5OH + NH_3} \xleftarrow{[H]} \underset{(A)}{[C_2H_5-O-N=O]} \xrightarrow{H_3O^+} \underset{(B)}{C_2H_5OH + HNO_2}$$

75. A is 

B is 

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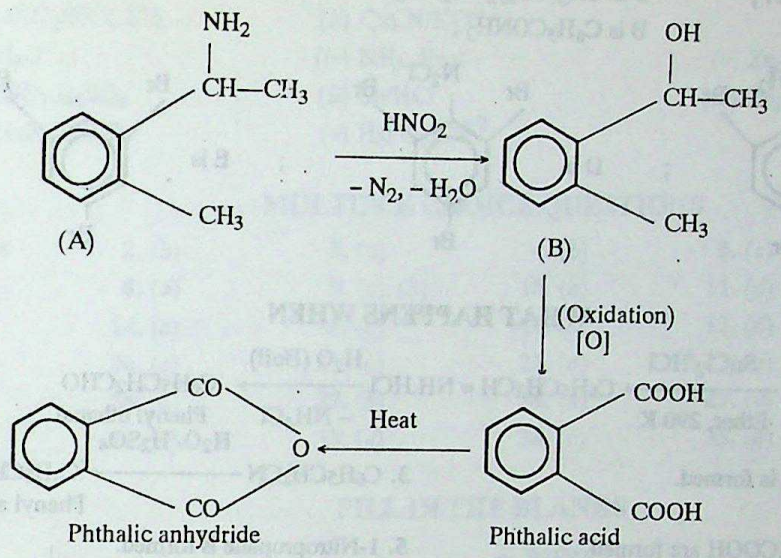
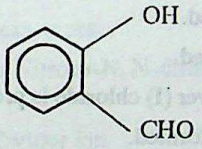
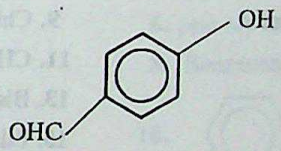
Sequence of reaction is



76. A is $C_6H_5NH_2$; B is C_6H_5OH ; C is C_6H_5NC ;

D is 

E is 

COMPLETING THE EQUATIONS

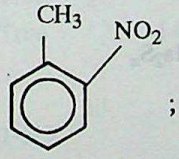
For Q. 1-23 refer to the chemical reactions of alkyl cyanides, nitro compounds and amines.

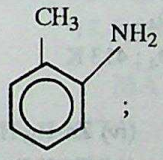
24. A is *m*-bromonitrobenzene ; B is *m*-bromoaniline ; C is *m*-bromobenzene diazonium chloride

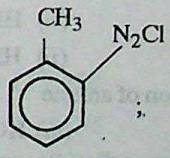
25. A is PCl_5 ; B is $C_6H_5CONH_2$; C is Br_2/KOH

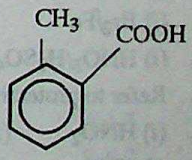
26. A is C_6H_5CN ; B is C_6H_5COOH

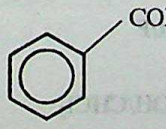
27. A is $C_6H_5CH_2NH_2$; B is $C_6H_5CH_2OH$

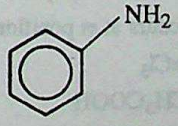
28. A is 

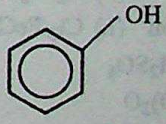
; B is 

; C is 

; D is 

29. A is 

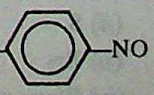
; B is 

; C is 

30. A is C_2H_5I ; B is C_2H_5NC ; C is $C_2H_5—N = C = S$

31. A is H_2SO_4/HNO_3 (nitrating mixture), B is $C_6H_5—\overset{\overset{O}{\uparrow}}{N} = N—C_6H_5$

32. A is $AgNO_2$(alc.) ; B is $(CH_3)_2C = O$

33. A is $C_6H_5NHCH_3$; B is $C_6H_5N(CH_3)_2$; C is $(CH_3)_2N$-  -NO

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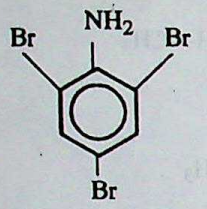
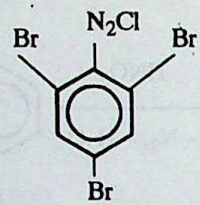
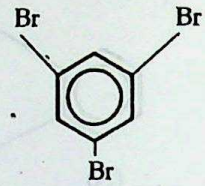
34. A is $CH_3(CH_2)_2CN$; B is $CH_3(CH_2)_2CH_2NH_2$; C is $CH_3(CH_2)_3OH$

35. A is $C_6H_5NH_2$; B is $C_6H_5CONH_2$;

C is 

; D is 

; E is 

WHAT HAPPENS WHEN

1. $C_6H_5CH_2CN$ (Benzyl cyanide) $\xrightarrow[\text{Ether, 290 K}]{SnCl_2/HCl}$ $C_6H_5CH_2CH = NH.HCl$ $\xrightarrow[-NH_4Cl]{H_2O\ (Boil)}$ $C_6H_5CH_2CHO$ (Phenyl ethanal)

2. $CH_3—N = CCl_2$ is formed.

3. $C_6H_5CH_2CN \xrightarrow{H_2O/H_2SO_4} C_6H_5CH_2COOH$ (Phenyl acetic acid)

4. $C_2H_5NH_2$ and HCOOH are formed.

5. 1-Nitropropane is formed.

6. 3-Nitro aniline is formed.

7. Mixture of *o*- and *p*-nitrotoluene is formed.

8. N-Methyl hydroxylamine is formed.

9. Chloropicrin is formed.

10. Acetic acid is formed.

11. $CH_3CH_2NH_2$ is formed.

12. $C_6H_5NH_2$ is formed.

13. Bis-(ethyl amine) silver (I) chloride is produced.

14. *n*-Propylamine is formed.

15. Ethylamine oxide is formed.

16. $C_6H_5CH_2NHC_6H_5$ is formed.

17. *p*-Nitroso-N, N-dimethyl aniline is formed

CONVERSIONS

Carry out the following steps :

1. (*i*) Sn/HCl (*ii*) $NaNO_2$/HCl, 278 K (*iii*) CuCN/KCN
2. (*i*) $NaNO_2$/HCl, 278 K (*ii*) phenol
3. (*i*) KCN (alc.) (*ii*) H_3O^+ (*iii*) NH_3, Heat (*iv*) KOH/Br_2
4. (*i*) Br_2/Fe (*ii*) HNO_3/H_2SO_4
5. (*i*) HNO_3/H_2SO_4 (*ii*) HNO_3/H_2SO_4 ; 413 K (*iii*) Na_2S_x
6. Refer to protective nitration of aniline
7. (*i*) HNO_2 (*ii*) P/Br_2 (*iii*) KCN (*iv*) Zn-Hg/HCl
8. (*i*) HNO_2 (*ii*) $K_2Cr_2O_7/H^+$ (*iii*) NH_3, Heat (*iv*) KOH/Br_2
9. (*i*) Oxidation (*ii*) $Cl_2/FeCl_3$ (Chlorination occurs at *m* position) (*iii*) HI/P
10. (*i*) HNO_3/H_2SO_4 (*ii*) $Cl_2/FeCl_3$
11. (*i*) $(CH_3CO)_2O$ (*ii*) Br_2/CH_3COOH
12. KOH/$CHCl_3$
13. (*i*) HNO_2 (*ii*) CH_3COOH/H_2SO_4
14. KOH/$CHCl_3$
15. (*i*) $NaNO_2$/HCl, 278 K (*ii*) CuCN/KCN
16. (*i*) H_2SO_4 (*ii*) Baking at 450 K
17. Reduction with Zn-Hg/HCl
18. (*i*) KOH/$CHCl_3$ (*ii*) HgO
19. (*i*) $NaNO_2$/HCl, 278 K (*ii*) HBF_4 (*iii*) Heat
20. (*i*) $NaNO_2$/HCl, 278 K (*ii*) S
21. Warm with water
22. (*i*) Nitration (*ii*) Br_2 (*iii*) $NaNO_2$/HCl, 278 K (*iv*) Warm with H_2O

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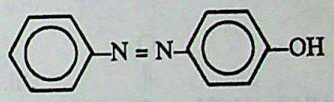
23. (*i*) $NaNO_2/HCl$, 278 (*ii*) CuCN/KCN (*iii*) H_3O^+
24. (*i*) $NaNO_2/HCl$, 278 (*ii*) CuCN/KCN (*iii*) H_3O^+ (*iv*) NH_3, Heat (*v*) Zn-Hg/HCl
25. (*i*) HNO_3/H_2SO_4 (*ii*) Sn/HCl (*iii*) Br_2 (*iv*) $NaNO_2/HCl$ (*v*) H_3PO_2/Cu^{+2}

MULTIPLE CHOICE QUESTIONS

1. (*b*) c	2. (*b*)	3. (*a*)	4. (*b*)	5. (*c*)	6. (*a*)
7. (*c*)	8. (*a*)	9. (*a*), (*b*)	10. (*b*)	11. (*d*)	12. (*b*)
13. (*b*)	14. (*c*)	15. (*c*)	16. (*c*)	17. (*d*)	18. (*b*)
19. (*b*)	20. (*c*)	21. (*c*)	22. (*d*)	23. (*a*)	24. (*d*)
25. (*b*)	26. (*a*)	27. (*b*)	28. (*b*)	29. (*d*)	30. (*a*)
31. (*a*)	32. (*d*)	33. (*d*)	34. (*c*)	35. (*d*).	

FILL IN THE BLANKS

1. less
2. isomers
3. not
4. ester
5. less, more
6. primary amino group
7. *p*-Nitroso-N, N-dimethyl aniline
8. Benzenamine and benzoyl chloride
9. Zwitter ion
10. 

11. Aldoximes
12. methyl isocyanate
13. Hypophosphorus acid
14. its controlled oxidation with Na_2CrO_4/H_2SO_4
15. 4-Aminophenol

TRUE AND FALSE STATEMENTS

1. False	2. True	3. False	4. False	5. False	6. True
7. True	8. False	9. False	10. True	11. False	12. True
13. True	14. True	15. False.			

MATCHING ITEMS

1-5-3	2-10-7	3-1-5	4-2-8
5-3-9	6-4-1	7-9-4	8-6-2
9-8-10	10-7-6		

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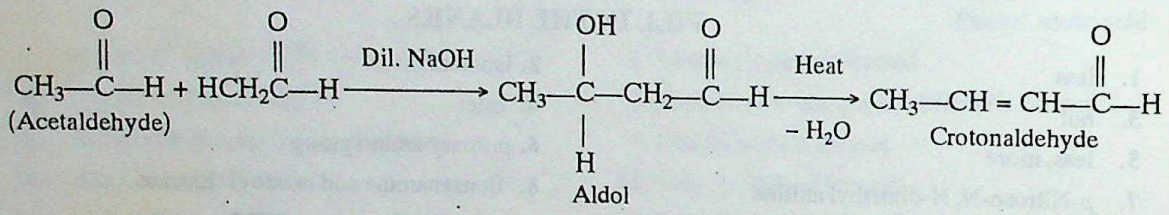
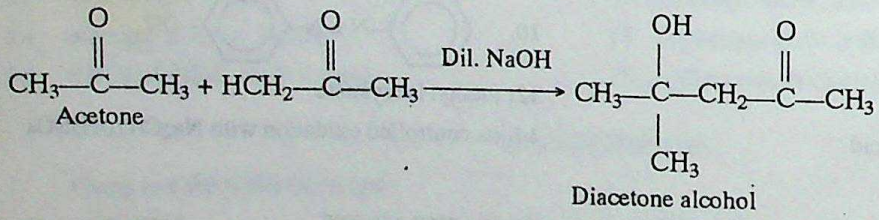
9A

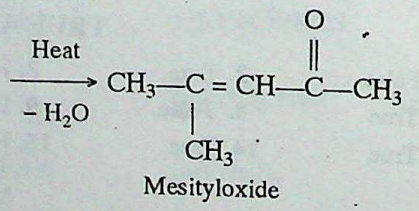
Organic Reactions and Organic Conversions

SOME IMPORTANT NAME REACTIONS

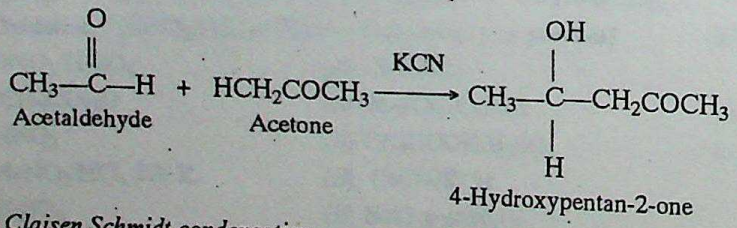
1. Aldol Condensation. It involves condensation reaction between two *aldehyde molecules* or *two ketone molecules* containing α-H atom in the presence of dilute alkali. The product is *β-hydroxy carbonyl compound* which on heating produces α, β-*unsaturated alehyde or ketone.*







When molecules of two different aldehydes or ketones undergo aldol type condensation, the reaction is called **crossed aldol condensation.**



**See also Claisen Schmidt condensation.*

2. Acyloin condensation. Acyloin is α-hydroxy ketone. Acyloins are produced when aliphatic carboxylic esters preferably methyl or ethyl esters are treated with sodium in an inert solvent like ether, benzene or toluene followed by treatment with acid.

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$$\underset{\text{Ethyl acetate}}{2CH_3COOC_2H_5} \xrightarrow{2Na,\ Ether} \underset{\text{Diketone}}{CH_3\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3} + 2C_2H_5ONa$$

$$CH_3-\overset{O}{\overset{\|}{C}}-\overset{O}{\overset{\|}{C}}-CH_3 \xrightarrow[\text{Acid}]{2H^+} \underset{\text{Acyloin}}{CH_3-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}H}-CH_3}$$

3. Arndt-Eistert-Synthesis. It involves the conversion of carboxylic acid into next higher homologue, *i.e.*, **RCOOH** to **RCH_2COOH**. The various steps are

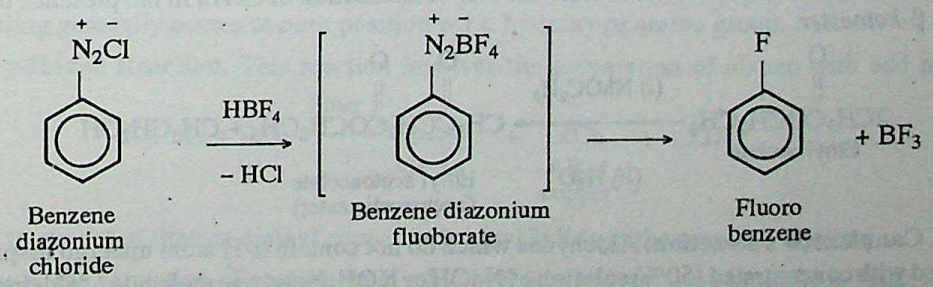
$$R-\overset{O}{\overset{\|}{C}}-OH \xrightarrow{PCl_5} \underset{\text{Acid chloride}}{R-\overset{O}{\overset{\|}{C}}-Cl} \xrightarrow[-HCl]{CH_2N_2} \underset{\text{Diazoketone}}{R-\overset{O}{\overset{\|}{C}}-CHN_2}$$

$$R-\overset{O}{\overset{\|}{C}}-CHN_2 \xrightarrow[\text{Rearangement}\ -N_2]{Ag_2O} \underset{\text{Ketene}}{R-CH=C=O} \xrightarrow{H_2O} \underset{\text{Acid}}{R-CH_2COOH}$$

4. Benzion Condensation. It involves the condensation between two molecules of *benzaldehyde* in the presence of ethanolic solution of *KCN*.

$$\underset{\text{Benzaldehyde}}{2C_6H_5\underset{H}{\underset{|}{C}}=O} \xrightarrow[\text{Heat}]{KCN\ (alcohol)} \underset{\text{Benzoin}}{C_6H_5-\overset{O}{\overset{\|}{C}}-\overset{OH}{\overset{|}{C}}-C_6H_5}\ (H)$$

5. Balz-Schiemann's Reaction. This reaction involves the conversion of ***aryl diazonium halide*** to ***aryl fluoride*** by treatment with *fluoboric acid (HBF_4)*



6. Bouveault-Blanc Reduction. It involves the reduction of ***esters*** to ***alcohols*** by using sodium alcohol as the reducing agent.

$$\underset{\text{Ethyl acetate}}{CH_3COOC_2H_5} \xrightarrow[2[H]]{Na/alcohol} C_2H_5OH + CH_3CH_2OH$$

7. Birch Reduction. It involves the reduction of *C = C bond* by using sodium in liquid ammonia in the presence of alcohol.

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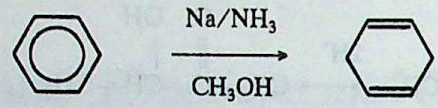
$$R—CH = CH_2 \xrightarrow[2[H]]{Na/NH_3} R—CH_2CH_3$$

Benzene which is not reduced by Zn-Hg/HCl or Na/alcohol can be reduced by Birch reduction



Benzene 1, 4-cyclohexadiene

8. Baeyer Villiger oxidation. It involves the oxidation of ketones with organic peroxy acid like *perbenzoic acid* $C_6H_5CO_3H$ or *per acetic acid* (CH_3CO_3H) to form esters.

$$\underset{\text{Acetone}}{CH_3—\overset{\overset{O}{\|}}{C}—CH_3} \xrightarrow[(CH_3CO_3H)]{\text{Peracetic acid}} \underset{\text{Methyl acetate}}{CH_3—\overset{\overset{O}{\|}}{C}—OCH_3}$$

9. Brown Hydroboration. This involves addition of diborane (B_2H_6) to olefinic double bond to form triorganoborane which on subsequent treatment with $H_2O_2/\bar{O}H$ gives alcohol. This ultimately causes anti Markovnikoff's addition of H_2O across unsymmetrical C = C bond.

$$\underset{\text{Alkene}}{6R—CH = CH_2} + B_2H_6 \longrightarrow 2(R—CH_2—CH_2)_3B \xrightarrow[-2H_3BO_3]{H_2O_2/\bar{O}H} \underset{\text{Alcohol}}{6R—CH_2CH_2OH}$$

10. Claisen-Schmidt Condensation. It involves the condensation between *benzaldehyde* and *aliphatic aldehydes* in the presence of dilute alkali.

$$\underset{\text{Benzaldehyde}}{C_6H_5\underset{\underset{H}{|}}{C} = O} + \underset{\text{Acetaldehyde}}{HCH_2CHO} \xrightarrow{\text{Dil. HaOH}} \left[\underset{\text{(Unstable, mixed aldol)}}{C_6H_5\overset{\overset{OH}{|}}{C}H—CH_2—CHO}\right] \xrightarrow{-H_2O} \underset{\text{Cinnamaldehyde}}{C_6H_5CH = CH—CHO}$$

11. Claisen Condensation. It involes the self-condensation of ***esters*** in the presence of ***alkoxide base*** to produce β-***ketoester***.

$$\underset{\text{Ethyl acetate}}{2CH_3\overset{\overset{O}{\|}}{C}OCH_2CH_3} \xrightarrow[(ii)\ H_3O^+]{(i)\ NaOC_2H_5} \underset{\text{Ethyl acetoacetate (acetoacetic ester)}}{CH_3\overset{\overset{O}{\|}}{C}CH_2\overset{\overset{O}{\|}}{C}OCH_2CH_3} + CH_3CH_2OH$$

12. Cannizzaro's Reaction. Aldehydes which do not contain α-H atom undergo **disproportionation** when heated with concentrated (50%) solution of NaOH or KOH. Here, one molecule of aldehyde gets oxidised while the other is reduced.

$$\underset{\text{Formaldehyde}}{HCHO} + HCHO \xrightarrow{50\%\ NaOH} \underset{\text{Sod. formate}}{HCOONa} + \underset{\text{Methyl alcohol}}{CH_3OH}$$

$$\underset{\text{Bezaldehyde}}{C_6H_5CHO} + C_6H_5CHO \xrightarrow{50\%\ NaOH} \underset{\text{Sodium benzoate}}{C_6H_5COONa} + \underset{\text{Benzyl alcohol}}{C_6H_5CH_2OH}$$

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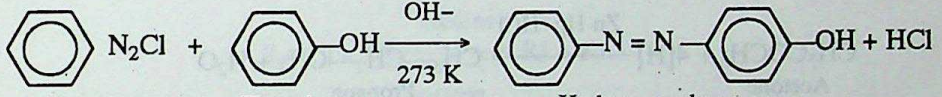
$$\underset{\text{2, 2-Dimethyl propanal}}{2(CH_3)_3C.CHO} \xrightarrow{50\%\ NaOH} \underset{\text{Sod. 2, 2-Dimethyl Propanoate}}{(CH_3)_3C.COONa} + \underset{\text{2, 2-Dimethyl-1-propanol}}{(CH_3)_3C.CH_2OH}$$

13. Carbylamine Reaction. It is a chemical reaction between ***primary amines*** and ***chloroform*** in the presence of NaOH or KOH to form ***carbylamines.***

$$\underset{\text{Ethyl amine}}{C_2H_5NH_2} + \underset{\text{Chloroform}}{Cl_3CH} + 3KOH \longrightarrow \underset{\text{Ethyl-isocyanide}}{C_2H_5N \rightleftarrows C} + 3KCl + 3H_2O$$

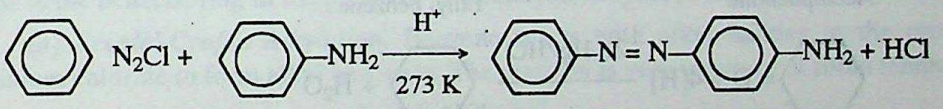
$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Chloroform}}{Cl_3CH} + 3KOH \longrightarrow \underset{\text{Phenyl isocyanide}}{C_6H_5N \rightleftarrows C} + 3KCl + 3H_2O$$

14. Coupling Reaction. It involves the reaction of diazonium salts with ***phenols*** or ***aromatic amino*** compounds under suitable conditions giving products of the general formula Ar—N = N—Ar, called *azo compounds.* Coupling with phenols takes place in mild *alkaline solution* while that with amines in mild *acidic solution.*



Benzene diazonium chloride — Phenol — *p*-Hydroxy azobenzene (orange dye)

(*i*) *Reaction with phenol*



Aniline — *p*-Aminoazobenzene (yellow dye)

(*ii*) *Reaction with aniline*

The coupling generally occurs at *para* position w.r.t. hydroxy or amino group.

15. Corey-House Reaction. This reaction involves the preparation of alkane with odd number of

$$R_2CuLi + R'X \xrightarrow{\text{Ether}} \underset{\text{Alkane}}{R—R'} + \underset{\text{Alkyl copper}}{RCu} + LiX$$

carbon atoms by treatment of lithium dialkyl copper with alkyl halide in the presence of ether

For example, the formation of pentane from ethyl bromide and *n*-propyl bromide is being illustrated as follows.

$$\underset{\text{Ether}}{C_2H_5Br} \xrightarrow{Li} \underset{\text{Ethyl lithium}}{C_2H_5Li} \xrightarrow{CuI} \underset{\text{Lithium diethyl copper}}{(C_2H_5)_2CuLi}$$

$$(C_2H_5)_2CuLi + \underset{n\text{-Propyl bromide}}{CH_3CH_2CH_2Br} \xrightarrow{\text{Ether}} \underset{\text{Pentane}}{C_2H_5CH_2CH_2CH_3} + C_2H_5Cu + LiBr$$

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16. Curtius Reaction. Curtius reaction involves the conversion of *acid azide ($R—CON_3$)* into *primary amine*

$$\underset{\text{Acid azide}}{R—\overset{\overset{O}{\|}}{C}—N_3} \xrightarrow{CH_3OH} R—\overset{\overset{H}{|}}{N}—\overset{\overset{O}{\|}}{C}—OCH_3 \xrightarrow{NaOH} \underset{\text{1° Amine}}{R—NH_2}$$

Acid azide can be obtained from acid chlorides or esters by treatment with hydrazine ($NH_2—NH_2$)

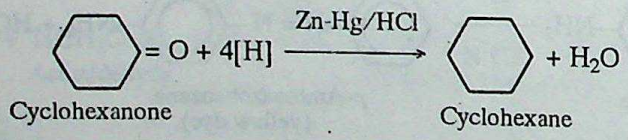
$$R—\overset{\overset{O}{\|}}{C}—Cl \xrightarrow{NH_2-NH_2} R—\overset{\overset{O}{\|}}{C}—NH—NH_2 \xrightarrow{HNO_2} \underset{\text{Acid azide}}{R—\overset{\overset{O}{\|}}{C}—N_3}$$

17. Clemmensen Reduction Reaction. This involves the reduction of *aldehyde* or *ketone* with *zinc-mercury amalgam and conc. hydrochloric acid* to give *hydrocarbons.* For example,

$$\underset{\text{Acetaldehyde}}{CH_3CHO} + 4[H] \xrightarrow{Zn\text{-}Hg/HCl} \underset{\text{Ethane}}{CH_3—CH_3} + H_2O$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 4[H] \xrightarrow{Zn\text{-}Hg/HCl} \underset{\text{Propane}}{CH_3—CH_2—CH_3} + H_2O$$

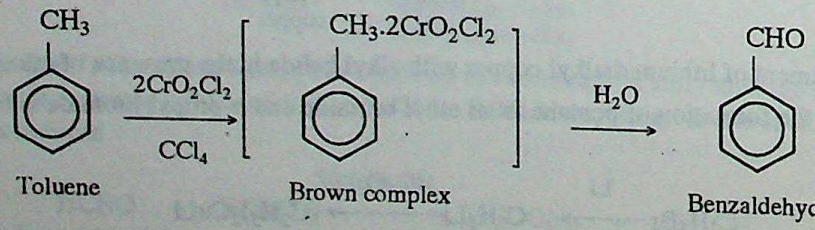
$$\underset{\text{Acetophenone}}{C_6H_5COCH_3} + 4[H] \xrightarrow{Zn\text{-}Hg/HCl} \underset{\text{Ethyl benzene}}{C_6H_5CH_2CH_3} + H_2O$$



18. Darzen Reaction. It involves the reaction of **straight chain primary alcohols** with **thionyl chloride** to form **choro derivative** without rearrangement.

$$ROH + SOCl_2 \xrightarrow{Pyridine} RCl + SO_2 + HCl$$

19. Etard's Reaction. This reaction involves the partial oxidation of ***toluene*** with ***chromyl chloride*** *(CrO_2Cl_2)* solution in CCl_4 or CS_2. The product formed is ***benzaldehyde.***



20. Elb's Reaction. This reaction involves the oxidation of phenol by potassium per sulphate to form a mixture of catechol and *p*-quinol

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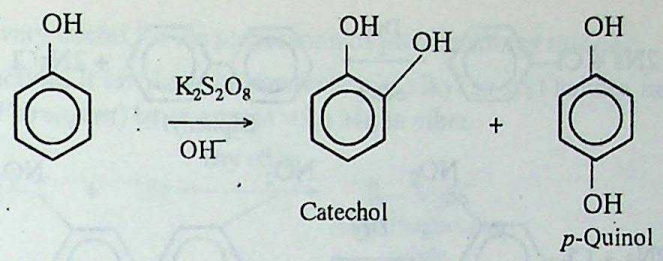


21. Esterification Reaction. This involves the formation of esters by reaction with carboxylic acids and alcohols in the presence of sulphuric acid.

$$\underset{\text{Acid}}{R-\overset{O}{\overset{\|}{C}}-OH} + \underset{\text{Alcohol}}{HOR'} \xrightarrow{H_2SO_4} \underset{\text{Ester}}{R-\overset{O}{\overset{\|}{C}}-OR'} + H_2O$$

$$\underset{\text{Benzoic acid}}{C_6H_5COOH} + HOCH_3 \longrightarrow \underset{\text{Methyl benzoate}}{C_6H_5COOCH_3} + H_2O$$

22. Finkelstein Reaction. This reaction involves the exchange of chloro or bromo group of alkyl halides with *iodo group* by treatment with postassium iodide (KI) in acetone or methanol.

$$R-Cl + KI \xrightarrow{\text{acetone}} RI + KCl$$

$$R-Br + KI \xrightarrow{\text{acetone}} RI + KBr$$

23. Friedel-Craft Reaction. This reaction involves the introduction of alkyl (R—) or acyl (RCO—) groups in the benzene ring in the presence of a catalyst, anhydrous aluminium chloride.

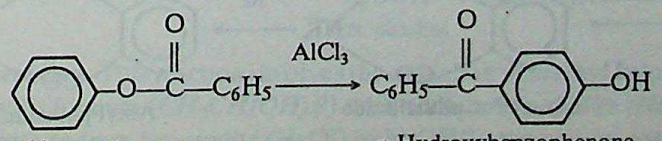
(*a*) *Friedel-Craft's Alkylation.* Benzene reacts with alkyl halides in the presence of anhydrous aluminium chloride to form alkyl benzenes. The reaction is very vigorous at room temperature.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow{\text{Anhyd. } AlCl_3} \underset{\text{Toluene}}{C_6H_5-CH_3} + HCl$$

(*b*) *Friedel-Craft's Acylation.* It involves introduction of acyl group in benzene ring and is affected by *acid chlorides*. The product is a ketone.

$$\underset{\text{Benzene}}{C_6H_6} + \underset{\text{Acid chloride}}{RCOCl} \xrightarrow{\text{Anhyd. } AlCl_3} \underset{\text{Ketone}}{C_6H_5COR} + HCl$$

24. Fries Rearrangement. It involves the isomerisation of *aryl esters* to *aryl ketones* in the presence of *anhydrous aluminium chloride.*



Phenyl benzoate p-Hydroxybenzophenone

25. Fittig Reaction. This reaction involves the treatment of ***haloarene*** with ***metallic sodium*** in the presence of dry ether to form ***diphenyl***

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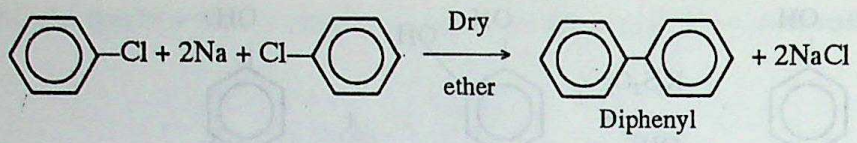
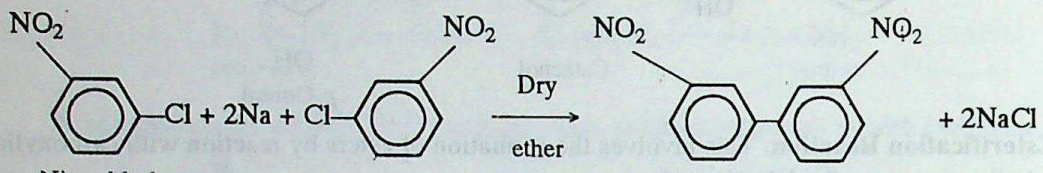
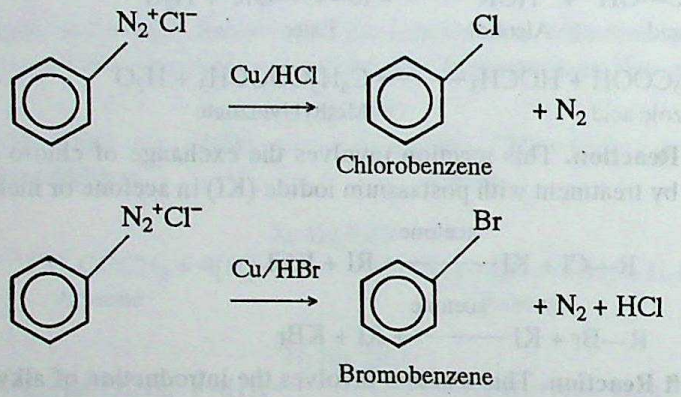




26. Gattermann Reaction. The reaction involves the preparation of ***chloro or bromo*** benzene from benzene diazonium chloride by treatment with ***Cu/HCl*** or ***Cu/HBr*** respectively.

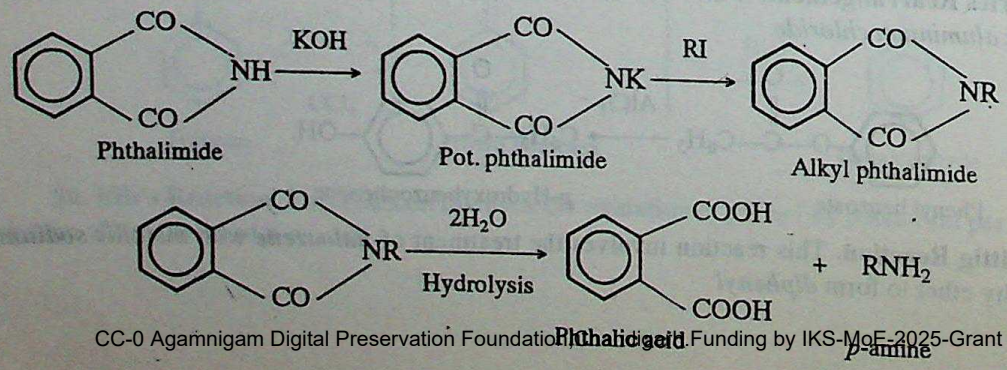


27. Gattermann Koch Reaction. This is a method for direct introduction of ***—CHO*** group in the ***benzene ring i.e.***, formylation of benzene ring. It is a modification of Friedel-Craft's reaction. Here, a mixture of CO and HCl gases are passed through benzene containing anhydrous $AlCl_3$ and a small amount of CuCl.

$$CO + HCl \longrightarrow \underset{\text{Formyl chloride}}{HCOCl}$$

$$C_6H_6 + HCOCl \xrightarrow[\text{298 K, 70 atm.}]{AlCl_3,\ CuCl} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

28. Gabriel Phthalimide Synthesis. This reaction involves the preparation of ***1° amine*** from ***alkyl halide*** by the use of phthalimide. Here phthalimide is first converted into its potassium salt by treating it with alcoholic potassium hydroxide. The potassium phthalimide is then heated with alkyl halide to yield N-alkyl phthalimide which is subsequently hydrolysed to *phthalic acid* and *primary amine* by heating with HCl or KOH solution.



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Gabriel synthesis is very useful for the preparation of **pure primary amines.**

29. Grignard's Reaction. It involves the conversion of alkyl or aryl halides into organo magnesium halides (known as *Grignard's reagent*) by treatment with Mg in ether.

$$R\text{—}X + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Alkyl magnesium halide}}{R\text{—}MgX}$$

$$C_6H_5\text{—}Br + Mg \xrightarrow{\text{Dry ether}} \underset{\text{Phenyl magnesium halide}}{C_6H_5MgX}$$

The conversion of C_6H_5Cl into C_6H_5MgCl is affected in tetrahydrofuran solvent in place of ether. Grignard reagent can be further converted into large number of compounds by proper choice of reagent.

RMgX

- $\xrightarrow{H_2O}$ $\underset{\text{Alkane}}{RH} + Mg(OH)X$
- $\xrightarrow{R'OH}$ $\underset{\text{Alkane}}{RH} + Mg(OR')X$
- $\xrightarrow{R'NH_2}$ $\underset{\text{Alkane}}{RH} + Mg(NHR')X$
- $\xrightarrow[(ii)\ H_2O]{(i)\ CO_2}$ $\underset{\text{Acids}}{R\text{—}COOH} + Mg(OH)X$
- $\xrightarrow[(ii)\ H_2O]{(i)\ RCHO}$ $\underset{\text{Sec. Alcohol}}{R_2CHOH} + Mg(OH)X$
- $\xrightarrow[(ii)\ H_2O]{(i)\ R_2C=O}$ $\underset{\text{Tert. alcohol}}{R_3COH} + Mg(OH)X$
- $\xrightarrow[(ii)\ H_2O]{(i)\ RC\equiv N}$ $\underset{\text{Ketone}}{R_2C=O} + Mg(OH)X + NH_3$
- $\xrightarrow{(i)\ RCOOR'}$ $\underset{\text{Tert. alcohol}}{R_3COH} + Mg(OH)X$

30. Haloform Reaction. This reaction involves the oxidation of ***methyl ketones (CH₃COR)*** or ***ethanal*** or ***secondary alcohols*** with formula ***(CH₃CH(OH)R)*** with ***sodium hypohalite (NaOX).*** When the aforesaid compounds are treated with sodium hypoiodite (NaOI) or $NaOH/I_2$, the yellow ppt. of iodoform is produced, and the reaction is called **iodoform reaction.**

$$\underset{\text{Ethanol}}{CH_3CHO} + 3NaOI \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 2NaOH$$

$$\underset{\text{Acetone}}{CH_3COCH_3} + 3NaOI \longrightarrow \underset{\text{Iodoform}}{CHI_3} + CH_3COONa + 2NaOH$$

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31. Hell-Volhard-Zelinsky (HVZ) Reaction. This involves the substitution of chloro or bromo group at the α-C atom of carboxylic acids. The reaction takes place between aliphatic carboxylic acid and Cl_2 or Br_2 in the presence of red phosphorus.

$$\underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow[-HCl]{Cl_2, P} \underset{\text{Monochloro acetic acid}}{CH_2ClCOOH} \xrightarrow[-HCl]{Cl_2, P} \underset{\text{Dichloro acetic acid}}{Cl_2CHCOOH} \xrightarrow[-HCl]{Cl_2, P} \underset{\text{Trichloro acetic acid}}{Cl_3C.COOH}$$

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xrightarrow[-HBr]{Br_2, P} \underset{\text{2-Bromopropanoic acid}}{CH_3-\underset{\underset{Br}{|}}{CH}COOH} \xrightarrow[-HBr]{Br_2, P} \underset{\text{2, 2-Dibromo-propanoic acid}}{CH_3C(Br)_2COOH}$$

32. Hoffmann Bromamide Reaction. This reaction involves the conversion of ***amides*** into ***primary amines*** with one carbon atom less than the parent amide by treatment with *bromine and caustic soda* or *caustic potash*. Here, $RCONH_2$ gets converted into RNH_2.

$$\underset{\text{Acetamide}}{CH_3CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Methyl amine}}{CH_3NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

$$\underset{\text{Propanamide}}{CH_3CH_2CONH_2} + Br_2 + 4KOH \longrightarrow \underset{\text{Ethyl amine}}{C_2H_5NH_2} + K_2CO_3 + 2KBr + 2H_2O$$

33. Hoffmann Mustard Oil Reaction. This involves the reaction of a primary aliphatic amine with carbon disulphide on warming. Dithiocarbamic acid is first formed which decomposes on heating with mercuric chloride to give alkyl isothiocyanate having a characteristic smell like that of mustard oil. For example,

$$\underset{\text{Ethylamine}}{C_2H_5NH_2} + \underset{\text{Carbon disulphide}}{C(=S)=S} \longrightarrow \underset{\text{Dithioethyl carbamic acid}}{C_2H_5-NH-\overset{\overset{S}{\|}}{C}-SH} \xrightarrow[\text{Heat}]{HgCl_2} \underset{\text{Ethyl isothiocyanate}}{C_2H_5-N=C=S} + 2HCl + HgS$$

34. Hunsdiecker Reaction. It involves the preparation of ***alkyl halide*** from the ***silver salt of carboxylic acid*** by refluxing with Br_2 *in* CCl_4.

$$\underset{\text{Silver propionate}}{CH_3CH_2COOAg} + Br_2 \xrightarrow{CCl_4} CH_3CH_2Br + CO_2 + AgBr$$

This reaction can be used in descending of series.

**Also see Shimonini reaction for comparison.*

35. Hofmann's Ammonolysis. This reaction involves the treatment of ***alkyl halide*** with ***ammonia*** to form mixture of *p, sec, tert.* amines

$$RX \xrightarrow[-HX]{NH_3} \underset{1^\circ\text{ Amine}}{RNH_2} \xrightarrow[-HX]{RX} \underset{2^\circ\text{ Amine}}{R_2NH} \xrightarrow[-HX]{RX} \underset{3^\circ\text{ Amine}}{R_3N} \xrightarrow{RX} \underset{\text{Quaternary salt}}{[R_4N]^+X^-}$$

Treatment of amine with excess of CH_3I to *form quaternary salt is referred to as* **exhaustive methylation of amine.**

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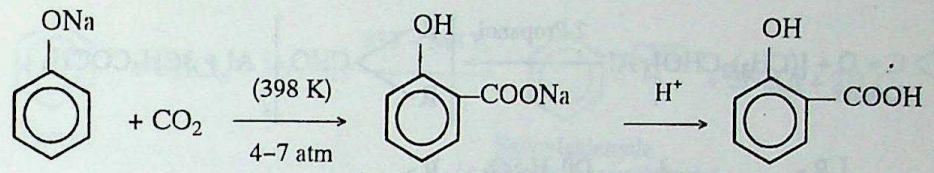
36. Kolbe's Reaction. This involves the reaction between ***sodium phenoxide*** and ***carbon dioxide*** under pressure (4—7 atmospheres) at 398 K to form ***sodium salicylate*** which on hydrolysis with mineral acids gives salicylic acid.



Sod. phenoxide — *o*-Sodium salicylate (*chief product*) — *o*-Salicylic acid

Although *p*-hydroxy benzoic acid (*p*-salicylic acid) is formed as a minor product, the separation of the two isomers can be carried out readily by steam distillation, *o*-isomer being more volatile.

37. Kolbe's Electrolytic Reaction. This reaction involves the electrolysis of an aqueous solution of sodium or potassium salt of carboxylic acid to give alkanes.

$$RCOOK \longrightarrow RCOO^- + K^+$$

At anode : $2R{-}COO^- \longrightarrow \underset{\text{Alkane}}{R{-}R} + 2CO_2 + 2e^-$

At cathode : $2H_2O + 2e^- \longrightarrow 2OH^- + H_2$

38. Leuckart Reaction. It involves the preparation of ***primary amine*** from ***aldehyde*** or ***ketone*** by treatment with ***ammonium formate*** or ***formamide*** followed by subsequent acid hydrolysis.

$$\underset{\text{Ald. or ketone}}{>C=O} + \underset{\text{Amm. formate}}{2HCOONH_4} \longrightarrow \underset{\text{N-Formyl amine}}{>CH{-}\overset{\overset{H}{|}}{N}{-}CHO} + CO_2 + NH_3 + 2H_2O \xrightarrow{H_2O/H^+} \underset{1^\circ\text{ Amine}}{>CH{-}NH_2} + HCOOH$$

39. Libermann nitroso Reaction. This reaction is given by both aliphatic and aromatic secondary amines which react with nitrous acid ($NaNO_2/HCl$) to give nitrosoamines which are yellow coloured oily compounds.

$$R_2NH + HONO \longrightarrow \underset{\text{Dialkyl nitrosoamine}}{R_2N{-}NO} + H_2O$$

The nitrosoamine on warming with a crystal of phenol and few drops concentrated H_2SO_4 gives green solution which on further treatment with aqueous alkali changes to deep blue colour. This reaction is used to distinguish *secondary amines* from *primary and tertiary amines*.

40. Mendius Reaction. This involves reduction of an alkyl or aryl cyanide with nascent hydrogen produced from sodium amalgam and alcohol. A primary amine is the product. For example,

$$CH_3CN + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Ethylamine}}{CH_3CH_2NH_2}$$

$$C_6H_5CN + 4[H] \xrightarrow{Na/C_2H_5OH} \underset{\text{Benzyl amine}}{C_6H_5CH_2NH_2}$$

Reduction may also be carried out by lithium aluminium hydride (LAH).

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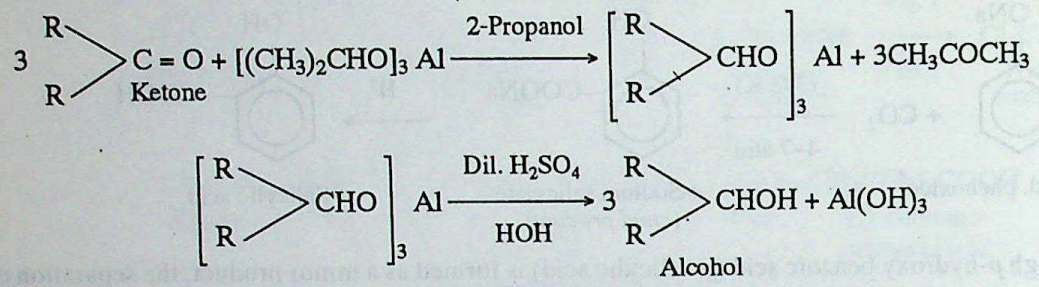
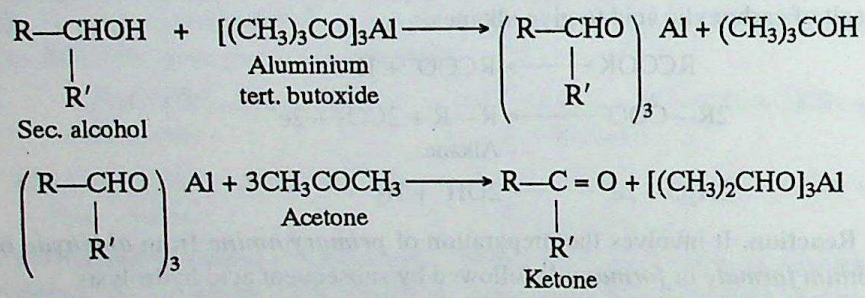
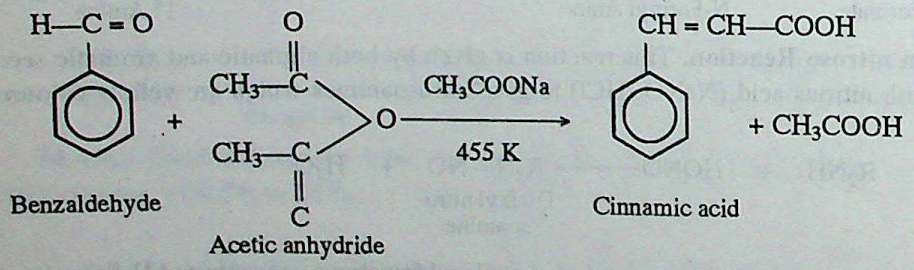
41. Meerwein-Ponndrof-Verley Reduction. This reaction involves the reduction of ***aldehyde*** or ***ketones*** to ***alcohols*** with ***aluminium isopropoxide*** in 2-propanol solution. The reducing agent is specific for ***C = O*** group to ***CHOH*** group but it does not reduce the other groups such as C = C or —NO_2 groups etc.



42. Oppenaur Oxidation. This is reverse of Meerwin Ponndrof reduction. It involves the oxidation of ***secondary alcohol*** with ***aluminium tertiary butoxide*** to ***ketone*** in acetone.



43. Perkin Reaction. It involves the reaction between aromatic aldehyde and an anhydride of aliphatic acid in the presence of sodium salt of the same acid. The product is α, β-unsaturated acid. For example, benzaldehyde and acetic anhydride give cinnamic acid.



44. Rosenmund Reaction. This reaction involves catalytic hydrogenation of acid chloride to yield aldehyde. The reduction is carried out by passing hydrogen gas through a hot solution of acid chloride in boiling xylene in the presence of palladium deposited on barium sulphate. The high reactivity of palladium as a catalyst is decreased by the presence of barium sulphate. This reaction is known as Rosenmund's reaction.

$$\underset{\text{Acid chloride}}{RCOCl} + H_2 \xrightarrow{Pd\text{-}BaSO_4} \underset{\text{Aldehyde}}{RCHO} + HCl$$

For example :

$$\underset{\text{Acetyl chloride}}{CH_3COCl} + H_2 \xrightarrow{Pd\text{-}BaSO_4} \underset{\text{Acetaldehyde}}{CH_3CHO} + HCl$$

$$\underset{\text{Benzoyl chloride}}{C_6H_5COCl} + H_2 \xrightarrow{Pb\text{-}BaSO_4} \underset{\text{Benzaldehyde}}{C_6H_5CHO} + HCl$$

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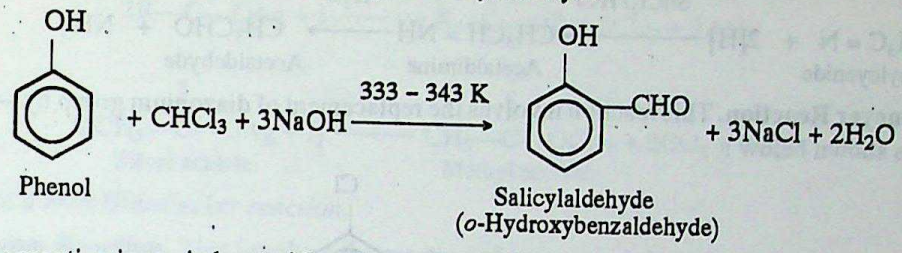
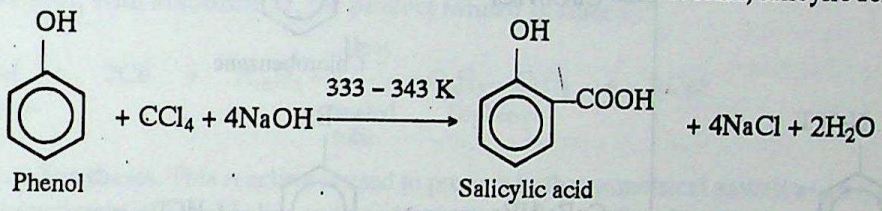
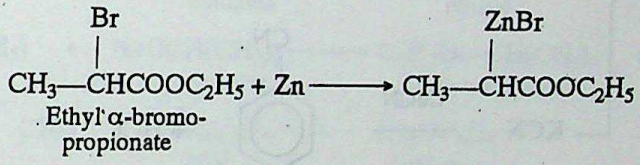
45. Reimer-Tiemann Reaction. This involves the reaction between phenol and chloroform in the presence of aqueous alkali at 333-343 K to give salicylaldehyde.

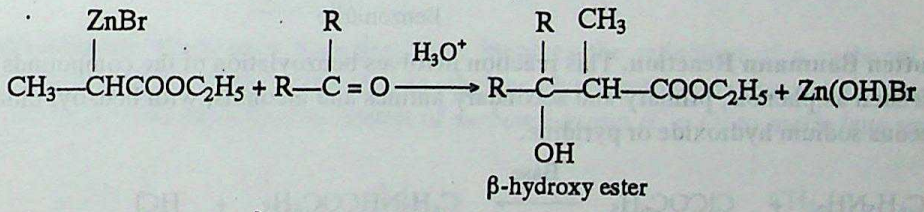


If the reaction is carried out with carbon tetrachloride, instead of chloroform, salicylic acid is produced.

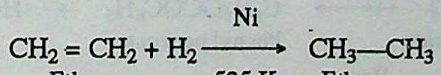


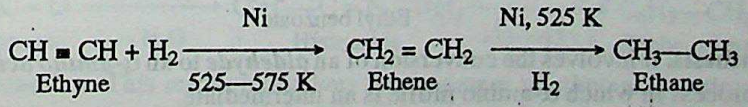
46. Reformatsky Reaction. This is a reaction between α-bromo ester and aldehyde or ketone in the presence of Zn to form β-hydroxy ester



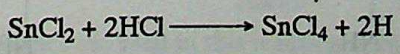


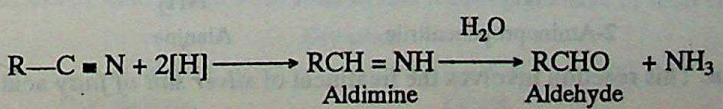
47. Sabatier and Sandarn's Reaction. This reaction involves the addition of hydrogen to unsaturated hydrocarbons in the presence of finely divided nickel at 475—575 K.





48. Stephen's Reduction Reaction. This reaction involves the reduction of *alky cyanides* with $SnCl_2$ and *hydrochloric acid* to give *aldimines* which on hydrolysis give *aldehydes*. In this reaction —*C ≡ N* group changes to —*CHO*





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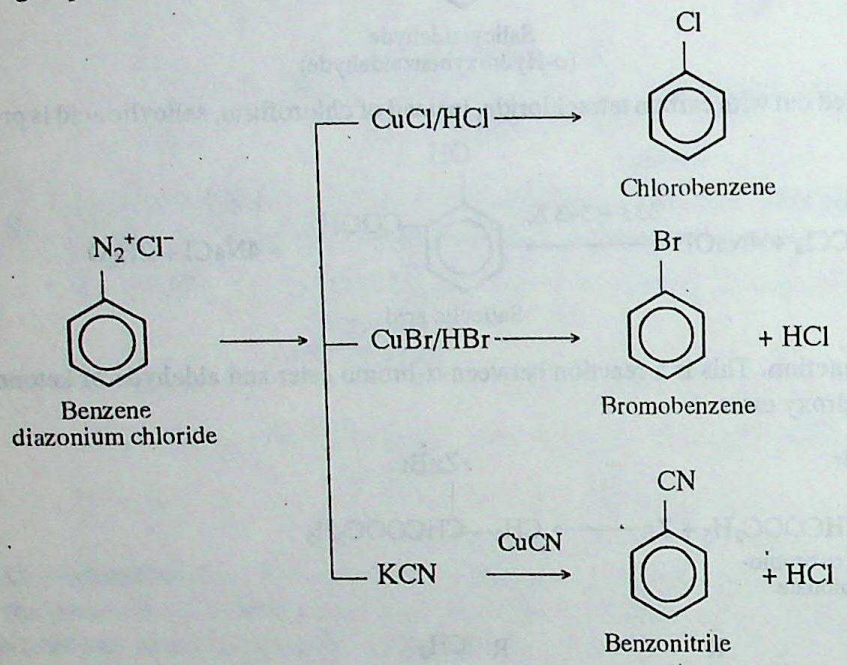
For example :

$$\underset{\text{Methylcyanide}}{CH_3C \equiv N} + 2[H] \xrightarrow{SnCl_2/HCl} \underset{\text{Acetaldimine}}{CH_3CH = NH} \xrightarrow{H_2O} \underset{\text{Acetaldehyde}}{CH_3CHO} + NH_3$$

49. Sandmeyer Reaction. This reaction involves the replacement of diazonium group by —Cl or —Br or —CN group as shown below :



50. Schotten Baumann Reaction. This reaction involves benzoylation of the compounds containing active hydrogen such as phenols, primary and secondary amines and alcohols, with benzoyl chloride in the presence of aqueous sodium hydroxide or pyridine.

$$\underset{\text{Aniline}}{C_6H_5NH_2} + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} \xrightarrow{\text{Base}} \underset{\text{Benzanilide}}{C_6H_5NHCOC_6H_5} + HCl$$

$$\underset{\text{Phenol}}{C_6H_5OH} + \underset{\text{Benzoyl chloride}}{ClCOC_6H_5} \xrightarrow{\text{Base}} \underset{\text{Phenyl benzoate}}{C_6H_5OCOC_6H_5} + HCl$$

$$\underset{\text{Ethyl alcohol}}{C_2H_5OH} + ClCOC_6H_5 \xrightarrow{\text{Base}} \underset{\text{Ethyl benzoate}}{C_6H_5COOC_2H_5} + HCl$$

51. Strecker's Synthesis. It involves the conversion of an ***aldehyde*** to an ***α-amino acid*** with one more carbon atom by two step process in which α-amino nitrile is an intermediate.

$$\underset{\text{Ethanal}}{CH_3\overset{\overset{O}{\|}}{C}H} \xrightarrow[NH_4Cl]{NaCN} \underset{\text{2-Aminopropanenitrile}}{CH_3CH(NH_2)C \equiv N} \xrightarrow{H_2O/H^+} \underset{\text{Alanine}}{CH_3CH(NH_2)COOH}$$

52. Simonini Reaction. This reaction involves the treatment of ***silver salt of fatty*** acid with ***iodine*** to form ***esters***.

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$$2R-\overset{\overset{\displaystyle O}{\|}}{C}-OAg + I_2 \longrightarrow R-\overset{\overset{\displaystyle O}{\|}}{C}-OR + 2CO_2 + 2AgI$$

$$\underset{\text{Silver acetate}}{2CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OAg} + I_2 \longrightarrow \underset{\text{Methyl acetate}}{CH_3-\overset{\overset{\displaystyle O}{\|}}{C}-OCH_3} + 2CO_2 + 2AgI$$

Compare it with Hinsdiecker reaction.

53. Ulmann Reaction. This involves the reaction of an *aryl iodide with copper powder* on heating in a sealed tube. For example, with iodobenzene, the product formed is diphenyl.

$$\underset{\text{Iodobenzene}}{C_6H_5I} + 2Cu + IC_6H_5 \xrightarrow[\text{Sealed tube}]{\text{Heat}} \underset{\text{Diphenyl}}{C_6H_5-C_6H_5} + 2CuI$$

54. Williamson Synthesis. This reaction is used to prepare both symmetrical as well as unsymmetrical ethers. It involves the treatment of alkyl halide with sodium alkoxide or sodium phenoxide.

$$CH_3I + \underset{\text{Sod. ethoxide}}{NaOC_2H_5} \longrightarrow \underset{\text{Methoxy-ethane}}{CH_3OC_2H_5} + NaI$$

$$C_2H_5I + \underset{\text{Sod. isopropoxide}}{NaOCH(CH_3)_2} \longrightarrow \underset{\text{2-Ethoxypropane}}{C_2H_5O-CH(CH_3)_2} + NaI$$

$$CH_3I + \underset{\text{Sod. phenoxide}}{NaOC_6H_5} \longrightarrow \underset{\text{Anisole}}{CH_3OC_6H_5}$$

55. Wolff Kishner Reduction Reaction. This involves the reduction of a carbonyl compound (aldehyde or ketone) in a high boiling solvent such as ethylene glycol with hydrazine and KOH or potassium *tert*-butoxide. The reaction involves the conversion of ***carbonyl group (C = O)*** to ***methylene group (CH_2)***. For example,

$$\underset{\text{Acetone}}{CH_3C(CH_3)=O} \xrightarrow[-H_2O]{NH_2-NH_2} \underset{\text{Hydrazone}}{CH_3-C(CH_3)=N-NH_2} \xrightarrow[453-473\ K]{KOH} \underset{\text{Propane}}{CH_3-CH_2} + N_2$$

$$\underset{\text{Benzophenone}}{C_6H_5-C(C_6H_5)=O} \xrightarrow[-H_2O]{NH_2-NH_2} \underset{\text{Hydrazone}}{C_6H_5-C(CH_3)=N-NH_2} \xrightarrow[453-473\ K]{KOH} \underset{\text{Diphenyl methane}}{C_6H_5-CH_2} + N_2$$

56. Wurtz Reaction. This reaction involves the treatment of ethereal solution of alkyl halides with metallic sodium to produce alkanes.

$$RX + 2Na + XR \xrightarrow{\text{Dry ether}} \underset{\text{Alkane}}{R-R} + 2NaX$$

Generally bromo or iodo alkanes are used in this reaction because of their relatively high reactivity.

$$\underset{\text{Iodo methane}}{2CH_3I} + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3-CH_3} + NaI$$

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If we start with different halides, the mixture of alkanes is obtained. For example, if we begin with CH_3I and C_2H_5I, a mixture of *propane, ethane* and *butane* is formed.

$$\underset{\text{Iodomethane}}{CH_3I} + 2Na + \underset{\text{Iodoethane}}{IC_2H_5} \xrightarrow{\text{Dry ether}} \underset{\text{Propane}}{CH_3—C_2H_5} + 2NaI$$

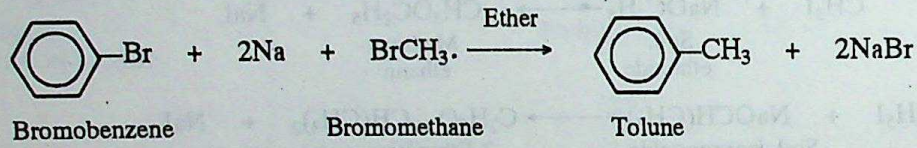
$$2CH_3I + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Ethane}}{CH_3—CH_3} + 2NaI$$

$$2C_2H_5I + 2Na \xrightarrow{\text{Dry ether}} \underset{\text{Butane}}{C_2H_5—C_2H_5} + 2NaI$$

Thus, Wurtz reaction is not suitable to prepare alkanes with odd number carbon atoms. Methane, however, cannot be prepared by this reaction at all.

However, *alkane with odd number carbons can be prepared with Corey House reaction.*

57. Wurtz-Fittig Reaction. This reaction is modification of Wurtz reaction to prepare aromatic hydrocarbons. Here ethereal solution of haloalkane and that of haloarene is treated with metallic sodium.



$C_6H_5—C_6H_5$ (Diphenyl) and $CH_3—CH_3$ (ethane) are side product of this reaction.

DISTINCTION BETWEEN SOME PAIRS OF COMPOUNDS

1. Chlorobenzene (C_6H_5Cl) and Benzyl Choride ($C_6H_5CH_2Cl$) *(Pb. Board 1989 ; H.P. 1992)*

Benzyl chloride behaves like aliphatic halides. When it is allowed to react with aqueous solution of NaOH, the resulting solution gives white precipitates with $AgNO_3$ solution in the presence of dil HNO_3. *Chlorobenzene* on the other hand, does not give white precipitate with similar reagents.

$$\underset{\text{Benzyl chloride}}{C_6H_5CH_2Cl} \xrightarrow{NaOH(aq)} C_6H_5CH_2OH + NaCl$$

$$NaCl + AgNO_3 \longrightarrow \underset{\text{White ppt.}}{AgCl\downarrow} + NaNO_3$$

C_6H_5Cl does not react with NaOH at ordinary temperature.

Similar test can be used to distinguish between

(*a*) ***C_2H_5Cl and C_6H_5Cl***

C_2H_5Cl gives white ppt. while C_6H_5Cl does not.

(*b*) ***C_2H_5Cl and C_2H_5I***

C_2H_5Cl gives while ppt. while C_2H_5I gives yellow ppt. of AgI.

(*c*) ***C_2H_5Cl and $CH_2 = CHCl$*** (vinyl chloride)

C_2H_5Cl gives white precipitates while $CH_2 = CHCl$ does not react.

2. n-Propyl bromide ($CH_3CH_2CH_2Br$) and Allyl bromide ($CH_2 = CH—CH_2Br$) *(D.S.B. 1985)*

Allyl bromide being unsaturated decolourises bromine solution. The *n-propyl bromide* on the other hand, does not respond to this test for unsaturation.

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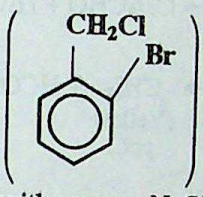
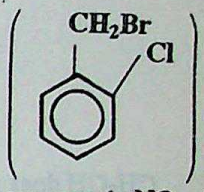
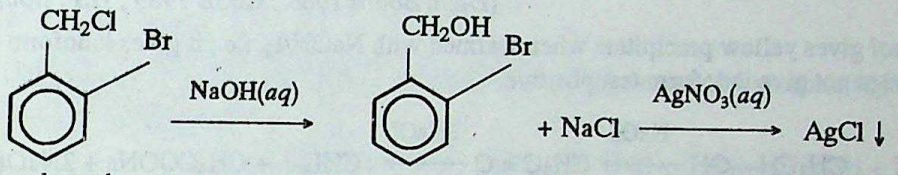
$$CH_2 = CH—CH_2Br \xrightarrow[CCl_4]{Br_2} CH_2(Br)—CH(Br)—CH_2Br$$

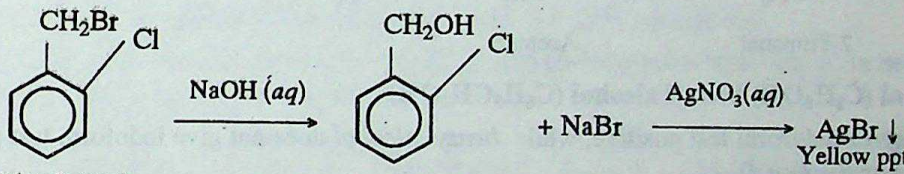
Allyl bromide — 1, 2, 3-Tribromopropane

3. o-Bromobenzyl chloride  **and o-chlorobenzyl bromide** 

o-Bromobenzyl chloride on, shaking with aqueous NaOH and subsequent treatment with aqueous $AgNO_3$ gives white precipitate of AgCl. *o-Chlorobenzyl bromide* on similar treatment produces dull yellow precipitate of AgBr.



o-Bromobenzyl chloride

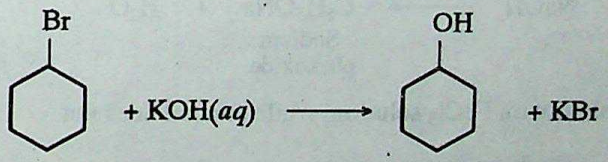


o-Chlorobenzyl bromide

4. Bromobenzene and Bromocyclohexane

A small quantity of aqueous KOH is added to both the compounds followed by acidification with HNO_3 and addition of silver nitrate solution.

Bromocyclohexane gives dull yellow ppt. of AgBr white bromobenzene does not react.



Cyclohexanol

$$KBr + AgNO_3 \longrightarrow KNO_3 + \underset{\text{Yellow}}{AgBr}$$

5. Carbon tetrachloride and chloroform *(Delhi Board 1988)*

Chloroform on warming with aniline in the presence of KOH gives repelling smell of phenyl isocyanide (carbylamine test) while CCl_4 does not respond to this test

$$CHCl_3 + C_6H_5NH_2 + 3KOH \xrightarrow{\text{Warm}} \underset{\text{Phenyl isocyanide}}{C_6H_5NC} + 3H_2O + 3KCl$$

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6. Methanol (CH_3OH) and Ethanol (C_2H_5OH)

(I.I.T. 1985 ; Delhi Board 1988, 89 ; Pb. Board 1991)

Ethanol gives iodoform test positive whereas *methanol* does not give any precipitate with I_2/NaOH.

$$\underset{\text{Ethanol}}{CH_3CH_2OH} + NaOI \xrightarrow{NaOH/I_2} CH_3CHO + H_2O + NaI$$

$$CH_3CHO + 3NaOI \longrightarrow \underset{\text{(Yellow ppt.)}}{CHI_3} + HCOONa + 2NaOH$$

CH_3OH does not respond to iodoform test.

7. 1-Propanol ($CH_3CH_2CH_2OH$) and 2-propanol [$(CH_3)_2CHOH$]

(Delhi Board 1988 ; CBSE 1989 ; H.P. Board 1988, 92)

2-Propanol gives yellow precipitate when warmed with NaOH/I_2, *i.e.*, it gives iodoform test positive but *1-propanol* does not give iodoform test positive.

$$\underset{\text{2-Propanal}}{CH_3\underset{\underset{CH_3}{|}}{CH}-OH} \xrightarrow[-H_2O,\ -NaI]{NaOI} \underset{\text{Acetone}}{CH_3\underset{\underset{CH_3}{|}}{C}=O} \xrightarrow{3NaOI} \underset{\text{Yellow ppt.}}{CHI_3} + CH_3COONa + 2NaOH$$

8. Ethanol (C_2H_5OH) benzyl alcohol ($C_6H_5CH_2OH$)

Ethanol gives iodoform test positive, while *benzyl alcohol* does not give iodoform test positive (*for reactions refer to distinction 4*).

9. Ethanol (C_2H_5OH) and phenol (C_6H_5OH)

(*i*) *Ethanol* gives iodoform test positive, while *phenol does not give yellow ppt*, in iodoform test.

(*ii*) *Ethanol* does not react with sodium hydroxide solution, while *phenol* neutralises sodium hydroxide solution:

$$C_6H_5OH + NaOH \longrightarrow \underset{\text{Sodium phenoxide}}{C_6H_5ONa} + H_2O$$

(*iii*) *Phenol* gives purple colour with $FeCl_3$ solution, while ethanol does not.

$$6C_6H_5OH + Fe^{3+} \longrightarrow \underset{\text{Purple}}{[Fe(OC_6H_5)_6]^{3-}} + 6H^+$$

This test can also be used to distinguish ***phenol*** and ***benzyl alcohol***. *Benzyl alcohol ($C_6H_5CH_2OH$) does not give purple colour with $FeCl_3$.*

10. Phenol (C_6H_5OH) and Cyclohexanol ($C_6H_{11}OH$)

(*i*) *Phenol* gives purple colour with $FeCl_3$ solution but *cyclohexanol* does not give purple colour with $FeCl_3$.

(*ii*) *Phenol* decolourises bromine water forming tribromophenol but *cyclohexanol* does not decolourise bromine water.

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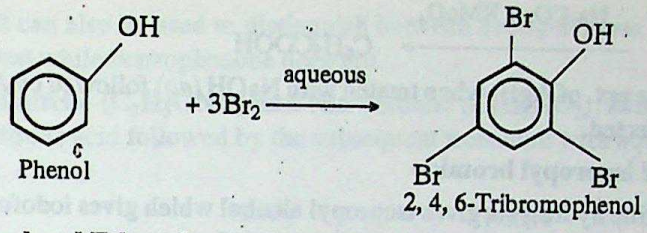

11. Ethanol and Ethanal

Ethanol gives hydrogen gas with sodium metal but ethanal does not

$$\underset{\text{Ethanol}}{C_2H_5OH} + Na \longrightarrow \underset{\text{Sodium ethoxide}}{C_2H_5ONa} + \tfrac{1}{2}H_2$$

CH_3CHO does not react with Na.

12. Ethanol and Benzyl alcohol

Ethanol gives yellow ppt. of CHI_3 with NaOI ($NaOH/I_2$) but benzyl alcohol ($C_6H_5CH_2OH$) does not give yellow ppt. with $NaOH/I_2$

$$C_2H_5OH + 4NaOI \longrightarrow \underset{\text{Yellow ppt.}}{CHI_3} + HCOONa + NaI + 2NaOH + 2H_2O$$

13. 1, 2-Dibromoethane ($CH_2Br.CH_2Br$) and 1, 1-Dibromoethane *(Pb. Board 1994)*

1, 1-Dibromoethane on treatment with KOH (*aq*) gives acetaldehyde which on heating with Tollen's reagent (amm. $AgNO_3$) gives silver mirror test.

$$\underset{\text{1, 1-Dibromoethane}}{CH_2CHBr_2} \xrightarrow{KOH\,(aq)} CH_3CH(OH)_2 \xrightarrow{-H_2O} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{\text{amm. } AgNO_3} \text{silver mirror}$$

1, 2-Dibromoethane on treatment with KOH (*aq*) gives ethylene glycol which gives pink colour with ceric ammonium nitrate.

$$\underset{\text{1, 2-Dibromoethane}}{CH_2BrCH_2Br} \xrightarrow{KOH\,(aq)} \underset{\text{Ethylene glycol}}{CH_2OH—CH_2OH} \xrightarrow[\text{nitrate}]{\text{Ceric amm.}} \text{Pink colour}$$

14. Bromobenzene (C_6H_5Br) and Ethyl bromide (C_2H_5Br) *(CBSE 1991)*

Ethyl bromide on treatment with aq. NaOH followed by aq. $AgNO_3$ gives precipitate of silver bromide but *bromobenzene* does not give any precipitate on similar treatment.

$$C_2H_5Br + NaOH\,(aq) \longrightarrow C_2H_5OH + NaBr$$

$$NaBr + AgNO_3 \longrightarrow AgBr\downarrow + NaNO_3$$

15. Chlorotoluene ($ClC_6H_4.CH_3$) and Benzyl bromide ($C_6H_5—CH_2Br$)

(*a*) On oxidation *chlorotoluene* gives chlorobenzoic acid which gives a green flame in Beilstein test.

$$\underset{\text{Chlorotoluene}}{Cl.C_6H_4.CH_3} \xrightarrow[KMnO_4 + Na_2CO_3]{[O]} \underset{\text{Chlorobenzoic acid}}{ClC_6H_4COOH}$$

Benzyl bromide on oxidation with alkaline $KMnO_4$ gives benzoic acid which does not give green flame in Beilstein test.

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$$C_6H_5CH_2Br \xrightarrow{Na_2CO_3 + KMnO_4} C_6H_5COOH$$

(*b*) *Benzyl bromide* gives the ppt. of AgBr when treated with NaOH (*aq*) followed by $AgNO_3$ treatment while *chlorotoluene* remains unaffected.

16. n-Propyl bromide and isopropyl bromide

Isopropyl bromide on alkaline hydrolysis gives isopropyl alcohol which gives iodoform test. *n*-Propyl bromide on hydrolysis gives *n*-propyl alcohol which does not give iodoform test.

$$\underset{\text{Isopropyl bromide}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-Br} \xrightarrow{KOH\ (aq)} \underset{\text{Isopropyl alcohol}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-OH} + KBr$$

$$CH_3-\overset{\overset{CH_3}{|}}{CH}-OH + 4NaIO \longrightarrow \underset{\text{Iodoform}}{CHI_3 \downarrow} + CH_3COONa + NaI + 2NaOH + 2H_2O$$

$$CH_3CH_2CH_2Br \xrightarrow[-KBr]{KOH\ (aq)} \underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH} \quad (\textit{does not give iodoform test})$$

17. 2-Pentanone ($CH_3COCH_2CH_2CH_3$) and 3-Pentanone ($C_2H_5COC_2H_5$)

2-Pentanone gives yellow ppt. of CHI_3 with NaOI, *i.e.*, it responds to iodoform test whereas *3-pentanone* fails to give yellow ppt.

$$\underset{\text{2-Pentanone}}{CH_3COCH_2CH_2CH_3} + 3NaOI \longrightarrow \underset{\text{ppt.}}{CHI_3} + CH_3CH_2COONa + 2NaOH$$

$C_2H_5COC_2H_5$ does not give iodoform test positive.

18. Propanal (CH_3CH_2CHO) and Propanone (CH_3COCH_3)

(*i*) *Propanone* gives iodoform test positive while *propanal* does not.

$$\underset{\text{Propanone}}{CH_3COCH_3} + 3NaOI \longrightarrow CHI_3 + CH_3COONa + 2NaOH$$

(*ii*) *Propanal* gives Tollen's test while *propanone* does not.

$$\underset{\text{Propanal}}{CH_3CH_2CHO} + 2[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow CH_3CH_2COOH + \underset{\text{Silver mirror}}{2Ag \downarrow} + 4NH_3 + H_2O$$

19. Formaldehyde (HCHO) and Acetaldehyde (CH_3CHO)

Acetaldehyde gives yellow ppt. with NaOI (Iodoform test) whereas *formaldehyde* fails to do so.

$$CH_3CHO + \underset{\text{Sodium hypoiodite}}{3NaOI} \longrightarrow \underset{\text{Iodoform}}{CHI_3 \downarrow} + HCOONa + 2NaOH$$

20. Acetaldehyde and Benzaldehyde (C_6H_5CHO)

Acetaldehyde gives yellow ppt. with NaOI (refer to distinction no. 19) while benzaldehyde does not give.

21. Benzaldehyde (C_6H_5CHO) and Acetophenone ($CH_3COC_6H_5$)

Acetophenone gives iodoform test (*i.e.* yellow ppt.) with NaOI whereas *benzaldehyde* does not.

$$\underset{\text{Acetophenone}}{CH_3COC_6H_5} + 3NaOI \longrightarrow C_6H_5COONa + \underset{\text{Yellow ppt.}}{CHI_3} + 2NaOH$$

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Same test can also be used to distinguish between ***acetophenone*** and ***benzophenone.*** Acetophenone gives iodoform test while benzophenone does not.

22. Ethyl nitrite (C_2H_5ONO) and Nitroethane ($C_2H_5NO_2$). *Nitroethane* gives blood red colour on treatment with nitrous acid followed by the subsequent treatment with aqueous NaOH. *Ethyl nitrite* does not give such colour.

$$\underset{\text{Nitroethane}}{C_2H_5NO_2} \xrightarrow{HNO_2} \underset{\underset{NOH}{\|}}{CH_3CNO_2} \xrightarrow{NaOH} \text{Red colour.}$$

23. Formic acid (HCOOH) and Acetic acid (CH_3COOH). *Formic acid* is a reducing agent. Hence. it gives Tollen's test positive, but *acetic acid* does not give Tollen's test.

$$HCOOH + 2[Ag(NH_3)_2]^+ + 2OH^- \longrightarrow 2H_2O + CO_2 + \underset{\text{Silver mirror}}{2Ag} + 4NH_3.$$

24. Benzoic acid and Phenol (*CBSE 1988 ; Delhi Board 1992 ; H.P. Board 1992*)

(*i*) Benzoic acid decomposes $NaHCO_3$ and gives efferevascence due to evolution of CO_2 but phenol does not decompose $NaHCO_3$

$$C_6H_5COOH + NaHCO_3 \longrightarrow C_6H_5COONa + CO_2 + H_2O$$

$$C_6H_5OH + NaHCO_3 \longrightarrow \text{No Reaction}$$

(*ii*) Phenol gives purple colouration with $FeCl_3$ but benzoic acid does not.

$NaHCO_3$ test can also be used to distinguish between ***acetic acid*** which decomposes $NaHCO_3$ and ***ethanol*** which does not.

25. Ethyl cyanide (C_2H_5CN) and Ethyl isocyanide ($C_2H_5N \rightleftharpoons C$). *Ethyl cyanide* on hydrolysis gives acetic acid whereas *ethyl isocyanide* gives formic acid which gives silver mirror test positive.

$$\underset{\text{Ethyl cyanide}}{C_2H_5CN} \xrightarrow[-NH_4Cl]{2H_2O/HCl} C_2H_5COOH$$

C_2H_5COOH does not give Tollen's test

$$\underset{\text{Ethyl isocyanide}}{C_2H_6N \rightleftharpoons C} + 2H_2O \xrightarrow{H^+} C_2H_5NH_2 + HCOOH$$

(*HCOOH gives Tollen's test positive*)

26. n-Propyl chloride ($CH_3CH_2CH_2Cl$) and Isopropyl chloride [$(CH_3)_2$ CHCl]. *Isopropyl chloride* on alkaline hydrolysis with aqueous KOH gives isopropyl alcohol which gives yellow ppt. with NaOI. *n*-Propyl chloride on the other hand, gives *n*-propyl alcohol which does not give iodoform test.

$$\underset{\text{Isopropyl chloride}}{CH_3\underset{\underset{Cl}{|}}{CH}CH_3} \xrightarrow{KOH\ (aq)} \underset{\text{Isopropyl alcohol}}{CH_3\underset{\underset{OH}{|}}{CH}CH_3} \quad \textit{(gives Iodoform test refer to No. 5)}$$

$$\underset{n\text{-Propyl chloride}}{CH_3CH_2CH_2Cl} \xrightarrow{KOH\ (aq)} \underset{n\text{-Propyl alcohol}}{CH_3CH_2CH_2OH}$$

(*does not respond to Iodoform test*)

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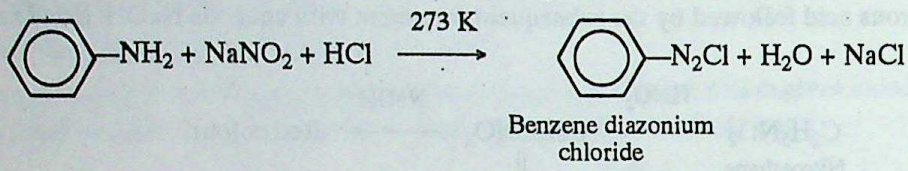
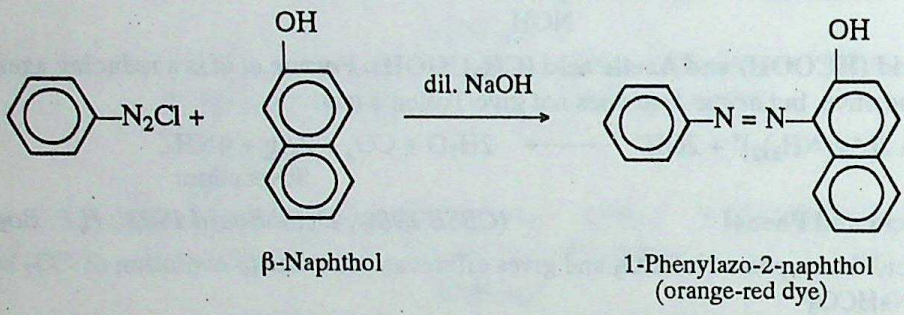
27. Ethyl amine and Aniline

Aniline forms diazonium salt with HNO_2 ($NaNO_2$/(HCl)) which give orange-red dye with phenolic compound. The phenolic compound used in this test is β-naphthol.





28. Ethyl amine and Diethyl amine

(*i*) *Carbylamine test.* Ethylamine gives ethyl isocyanide when treated with chloroform in the presence of KOH.

$$C_2H_5NH_2 + CHCl_3 + 3KOH \longrightarrow \underset{\text{Ethyl isocyanide}}{C_2H_5NC} + 3KCl + 3H_2O$$

Diethyl amine does not give this test.

(*ii*) *Hinsberg's test.* When treated with benzene sulphonyl chloride ($C_6H_5SO_2Cl$) also called Hinsberg's reagent, ethyl amine gives N-ethyl benzene sulphonamide which is soluble in aqueous KOH. Diethyl amine on the other hand, gives N, N-diethyl benzene sulphonamide which is insoluble in aqueous KOH.

$$C_6H_5SO_2Cl + \underset{\text{Ethyl amine}}{C_2H_5NH_2} \xrightarrow{-HCl} \underset{\text{(Soluble in aq. KOH)}}{C_6H_5SO_2NHC_2H_5}$$

$$C_6H_5SO_2Cl + (C_2H_5)_2NH \xrightarrow{-HCl} \underset{\text{(insoluble in aq. KOH)}}{C_6H_5SO_2N(C_2H_5)_2}$$

ORGANIC CONVERSIONS

Organic conversions basically refer to the conversion of one type of organic compound into another. They constitute important aspect of the study of organic chemistry. They require thorough understanding of the organic reactions and skill to interlink them. For the sake of simplicity let us study the basic procedure for conversion in three parts.

(A) *Aliphatic conversions.* (B) *Aromatic conversions* (C) *Mixed conversions*

A. ALIPHATIC CONVERSIONS

In general, the aliphatic conversions may be divided into three categories.

(*a*) **Ascent of Series.** They involve the conversion of lower members of the series to the higher members.

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(*b*) **Descent of Series.** They involve the conversion of higher members of series to the lower members

(*c*) **General Conversions.** They involve conversion from one family of compound into another.

(*a*) **The conversions based on ascent of series.**

These conversions involve any of the following reactions at some stage

(*i*) **Wurtz reaction**

$$\underset{\text{Alkyl halide}}{2R{-}X} \xrightarrow[\text{Dry Ether}]{Na} \underset{\text{Alkane}}{R{-}R} + 2NaX$$

This reaction can be employed if the number of carbon atoms in the desired product is double the number of carbon atoms in the starting compound. Let us study some examples.

Example 1. ***Ethane to Butane***

$$\underset{\text{Ethane}}{CH_3{-}CH_3} \xrightarrow[h\nu]{Cl_2} \underset{\text{Ethyl chloride}}{CH_3CH_2Cl} \xrightarrow{\text{Na, Ether}} \underset{\text{Butane}}{CH_3CH_2CH_2CH_3}$$

Example 2. ***Propene to n-hexane***

$$\underset{\text{Propene}}{CH_3CH = CH_2} \xrightarrow[\text{Org. Peroxide}]{HBr} \underset{n\text{-Propyl bromide}}{CH_3CH_2CH_2Br} \xrightarrow{\text{Na, Ether}} \underset{n\text{-Hexane}}{CH_3CH_2CH_2CH_2CH_2CH_3}$$

Example 3. ***Propene to 2, 3-Dimethylbutane***

$$\underset{\text{Propene}}{CH_3CH = CH_2} \xrightarrow{HBr} \underset{\text{Isopropyl bromide}}{CH_3\overset{\overset{CH_3}{|}}{C}H{-}Br} \xrightarrow{\text{Na, Ether}} \underset{\text{2, 3-Dimethyl butane}}{CH_3\overset{\overset{CH_3}{|}}{C}H{-}\overset{\overset{CH_3}{|}}{C}H{-}CH_3}$$

(*ii*) **Reaction of alkylhalide and potassium cyanide**

$$\underset{\text{Alkylhalide}}{R{-}X} + KCN\ (alc.) \longrightarrow \underset{\text{Alkyl cyanide}}{R{-}C{\equiv}N} + KX.$$

This reaction is generally used when the desired product has one carbon atom more than the parent compound in the chain. It may be noted that RCN can be further changed into $RCONH_2$, RCOOH, RCH_2NH_2, RCHO, etc., by suitable means (Refer to the properties of cyanide page 625). Let us study some conversions involving the use of cyanide reaction.

Example 4. ***Methyl alcohol to Ethyl alcohol***

$$\underset{\text{Methyl alcohol}}{CH_3OH} \xrightarrow{P/I_2} \underset{\text{Methyl iodide}}{CH_3I} \xrightarrow{KCN\ (alc.)} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{2H_2O/H^+} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethyl alcohol}}{CH_3CH_2OH}$$

Example 5. ***Ethanoic acid to Propanoic acid***

$$\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{P/I_2} \underset{\text{Ethyl Iodide}}{CH_3CH_2I}$$

$$\downarrow KCN\ (alc.)$$

$$\underset{\text{Propanoic acid}}{CH_3CH_2COOH} \xleftarrow{2H_2O/H^+} \underset{\text{Propanenitrile}}{CH_3CH_2CN}$$

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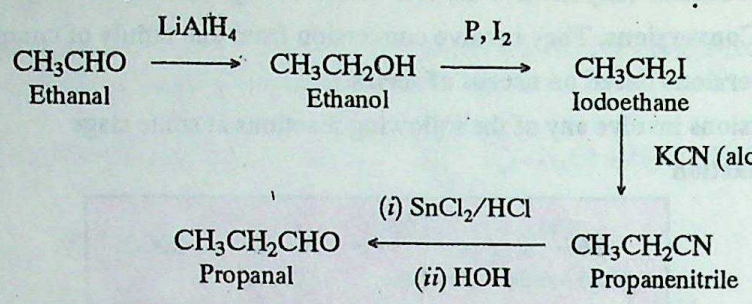
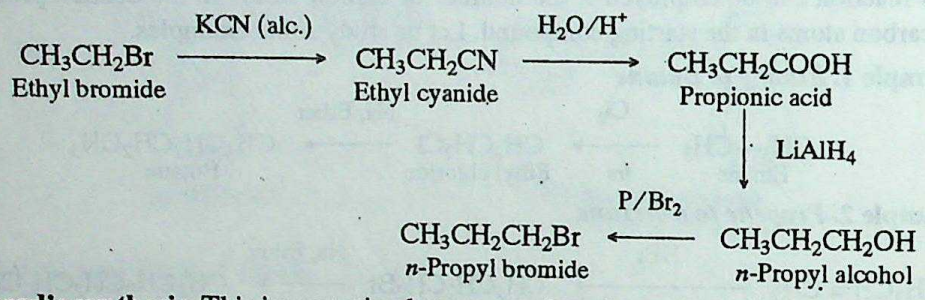
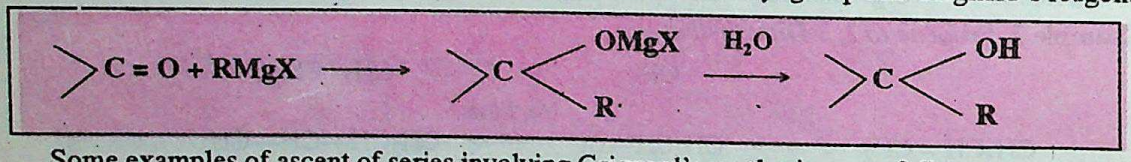
Example 6. ***Ethanal to Propanal***



Example 7. ***Ethyl bromide to n-propyl bromide***

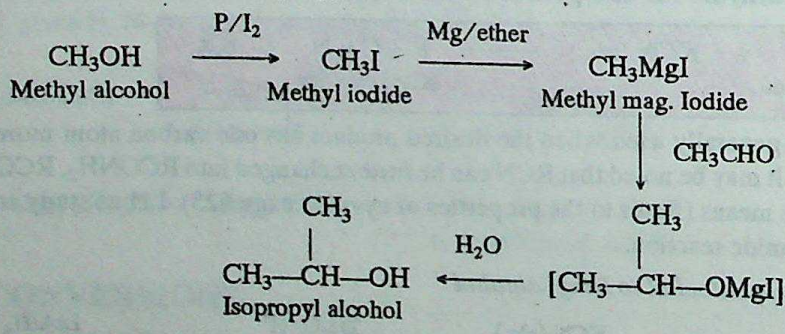


(*iii*) **Grignard's synthesis.** This is a reaction between carbonyl group and Grignard's reagent.

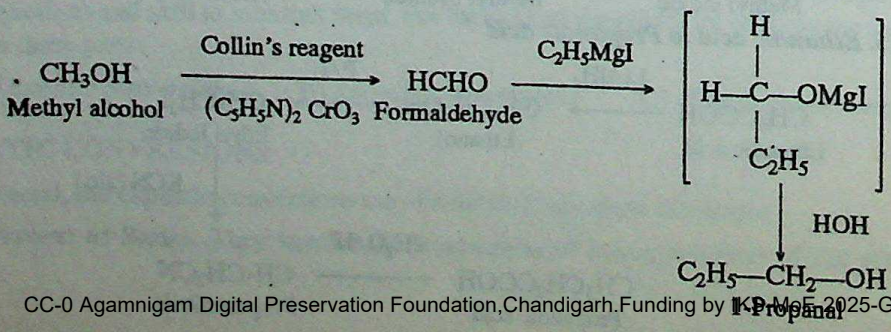


Some examples of ascent of series involving Grignard's synthesis are as follows :

Example 8. ***Methyl alcohol to isopropyl alcohol***



Example 9. ***Methyl alcohol to 1-Propanol***



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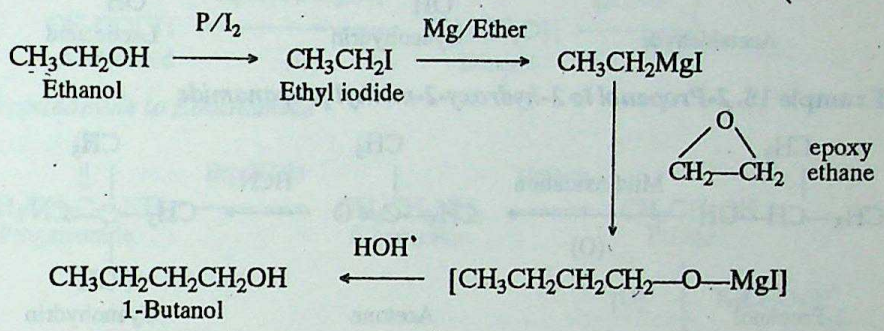
Example 10. ***Methanal to ethanal*** *(I.I.T. 1981)*

$$\underset{\text{Methanal}}{HCHO} \xrightarrow{CH_3MgI} [CH_3—CH_2—OMgI] \xrightarrow{H_2O} \underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow{(C_5H_5N)_2CrO_3} \underset{\text{Ethanal}}{CH_3CHO}$$

Example 11. ***Ethanol to 1-Butanol*** *(Dhanbad 1981)*



(*iv*) Reaction of alkyl halide and sodium acetylide

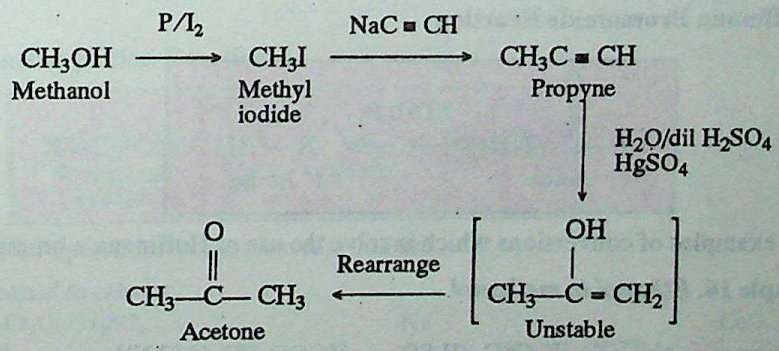
$$\underset{\text{Alkyl halide}}{R—X} + \underset{\text{Sodium acetylide}}{NaC \equiv CH} \longrightarrow \underset{\text{Higher alkyne}}{R—C \equiv CH} + NaX$$

Some examples of conversions utilising above reaction are :

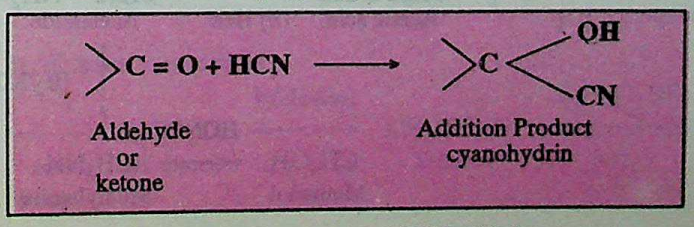
Example 12. ***Methane to propane***

$$\underset{\text{Methane}}{CH_4} \xrightarrow{Cl_2,\ h\nu} \underset{\text{Methyl chloride}}{CH_3Cl} \xrightarrow{NaC \equiv CH} \underset{\text{Propyne}}{CH_3C \equiv CH} \xrightarrow[450\ K]{H_2,\ Ni} \underset{\text{Propane}}{CH_3CH_2CH_3}$$

Example 13. ***Methanol to acetone***



(*v*) Addition of HCN to carbonyl group.



Some examples of the conversions utilising HCN addition are :

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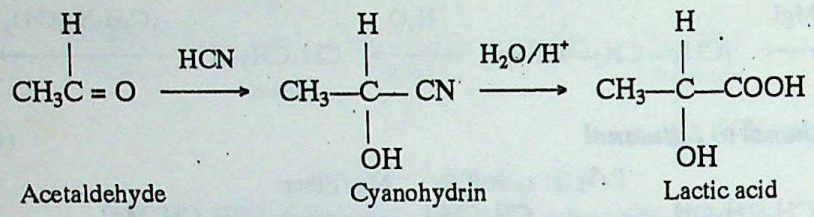
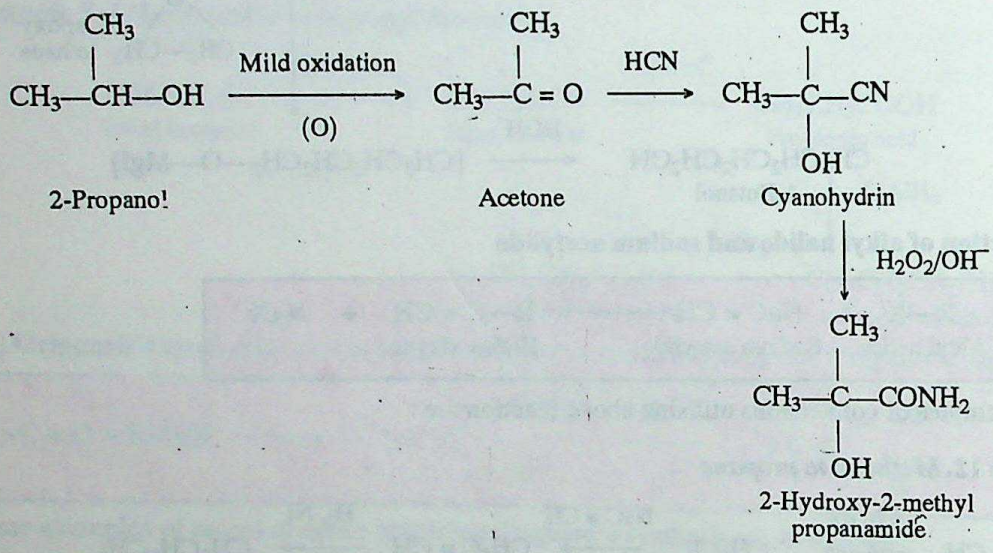
Example 14. ***Acetaldehyde to Lactic acid***



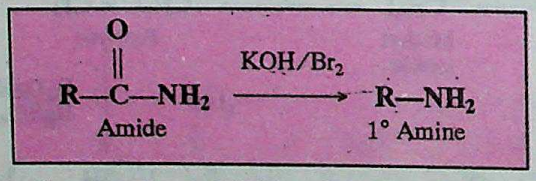
Example 15. ***2-Propanol to 2-hydroxy-2-methyl propanamide***



(*b*) **Conversions based upon descent of series**

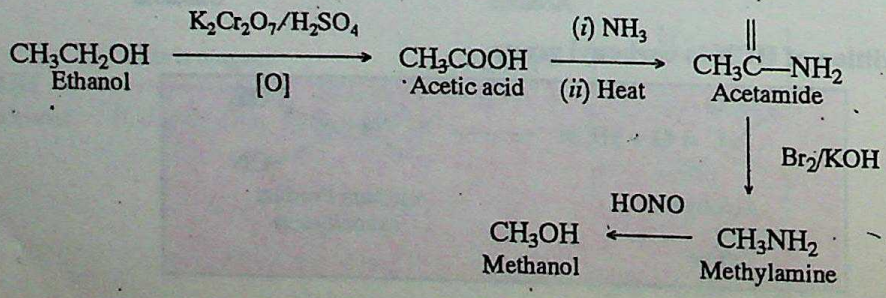
These conversions involve any of the following reactions at some stage

(*i*) **Hoffmann Bromamide Reaction**



Some examples of conversions which involve the use of Hoffmann's bromamide reaction are :

Example 16. ***Ethanol to methanol*** (*Delhi Board 1992*)



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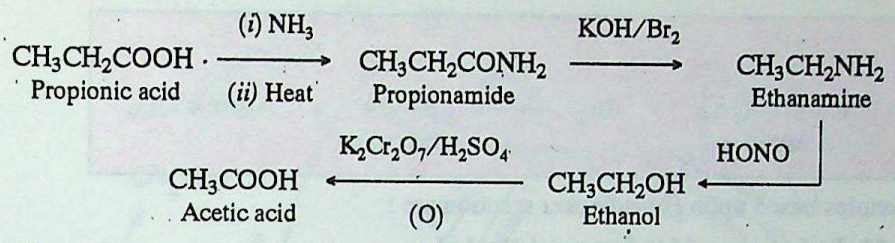
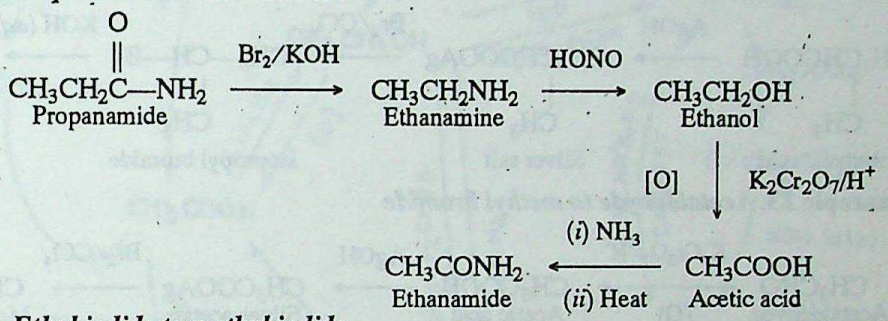
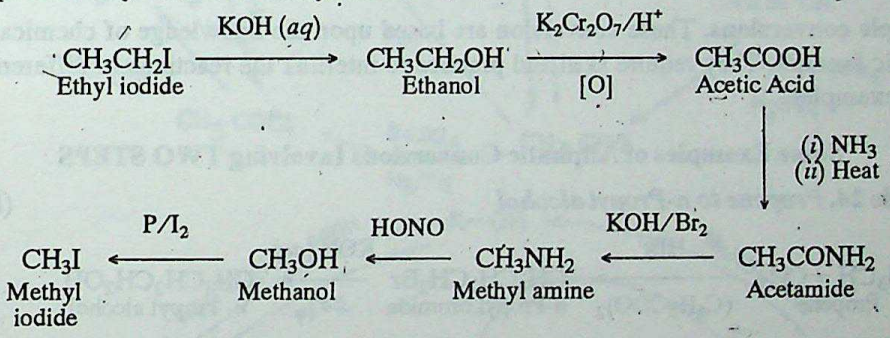
Example 17. ***Propionic acid to Acetic acid*** *(CBSE 1992, Delhi Board 1992, H.P. Board 1993)*



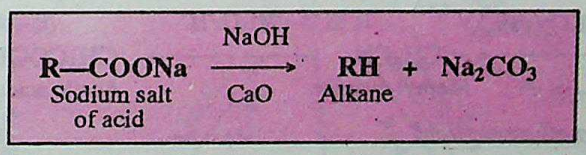
Example 18. ***Propanamide to Ethanamide***



Example 19. ***Ethyl iodide to methyl iodide***

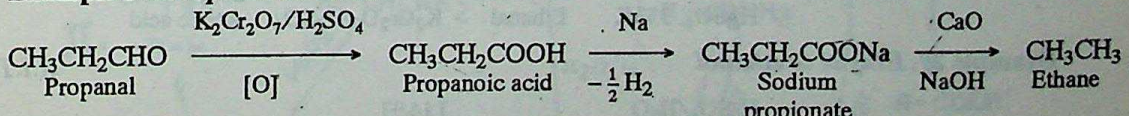


(*ii*) Sodalime Decarboxylation Reaction

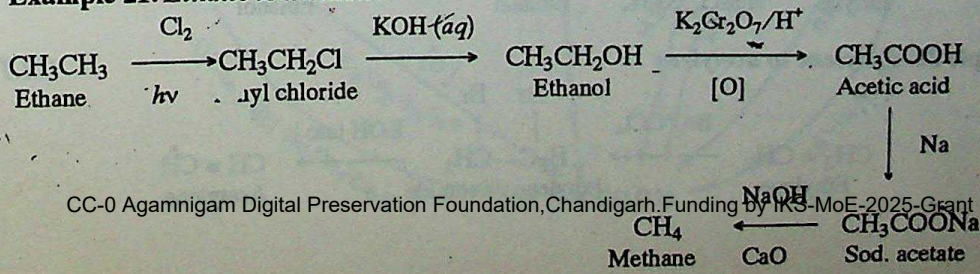


Some examples based upon decarboxylation reaction are :

Example 20. ***Propanal to ethane***



Example 21. ***Ethane to methane***



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(*iii*) Hunsdiecker Reaction

$$\underset{\text{Silver salt of acid}}{R-\overset{\overset{O}{\|}}{C}-OAg} + Br_2 \xrightarrow{CCl_4} \underset{\text{Alkyl halide}}{R-Br} + AgBr + CO_2$$

Some examples based upon Hunsdiecker reaction are :

Example 22. ***Isobutyric acid to isopropyl alcohol***

$$\underset{\text{Isobutyric acid}}{CH_3CH(CH_3)COOH} \xrightarrow{AgOH} \underset{\text{Silver salt}}{CH_3CH(CH_3)COOAg} \xrightarrow{Br_2/CCl_4} \underset{\text{Isopropyl bromide}}{CH_3-CH(CH_3)-Br} \xrightarrow{KOH\ (aq)} \underset{\text{Isopropyl alcohol}}{CH_3-CH(CH_3)-OH}$$

Example 23. ***Acetaldehyde to methyl bromide***

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[(O)]{K_2Cr_2O_7/H^+} \underset{\text{Acetic acid}}{CH_3COOH} \xrightarrow{AgOH} \underset{\text{Silver acetate}}{CH_3COOAg} \xrightarrow{Br_2/CCl_4} \underset{\text{Methyl bromide}}{CH_3Br} + CO_2$$

C. Simple conversions. These conversion are based upon the knowledge of chemical properties of different organic families. They require skill and practice to interlink the reactions of different families. Let us study some examples.

Some Examples of Aliphatic Conversions Involving TWO STEPS

Example 24. ***Propene to n-Propyl alcohol*** (*Roorkee 1984*)

$$\underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[(C_6H_5COO)_2]{HBr} \underset{n\text{-Propyl bromide}}{CH_3CH_2CH_2Br} \xrightarrow{KOH\ (aq)} \underset{n\text{- Propyl alcohol}}{CH_3CH_2CH_2OH}$$

Example 25. ***Methyl bromide to acetic acid*** (*I.I.T. 1982 ; Pb. Board 1988*)

$$\underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow{KCN\ (alc.)} \underset{\text{Methyl cyanide}}{CH_3CN} \xrightarrow{2H_2O/H^+} \underset{\text{Acetic acid}}{CH_3COOH}$$

Example 26. ***Ethyne to ethanoic acid*** (*CBSE 1987, 1993*)

$$CH\equiv CH \xrightarrow[HgSO_4,\ 333K]{H_2SO_4/H_2O} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow[K_2Cr_2O_7/H_2SO_4]{(O)} \underset{\text{Acetic acid}}{CH_3COOH}$$

Example 27. ***Ethyne to ethanol*** (*I.I.T. 1983*)

$$\underset{\text{Ethyne}}{CH\equiv CH} \xrightarrow[HgSO_4,\ 333K]{H_2SO_4/H_2O} \underset{\text{Ethanal}}{CH_3CHO} \xrightarrow{LiAlH_4} \underset{\text{Ethanol}}{CH_3CH_2OH}$$

Example 28. ***Ethylene to acetylene*** (*I.I.T. 1981*)

$$\underset{\text{Ethylene}}{CH_2=CH_2} \xrightarrow{Br_2/CCl_4} \underset{\text{Ethylene dibromide}}{H_2C(Br)-CH_2(Br)} \xrightarrow{KOH\ (alc.)} \underset{\text{Acetylene}}{CH\equiv CH}$$

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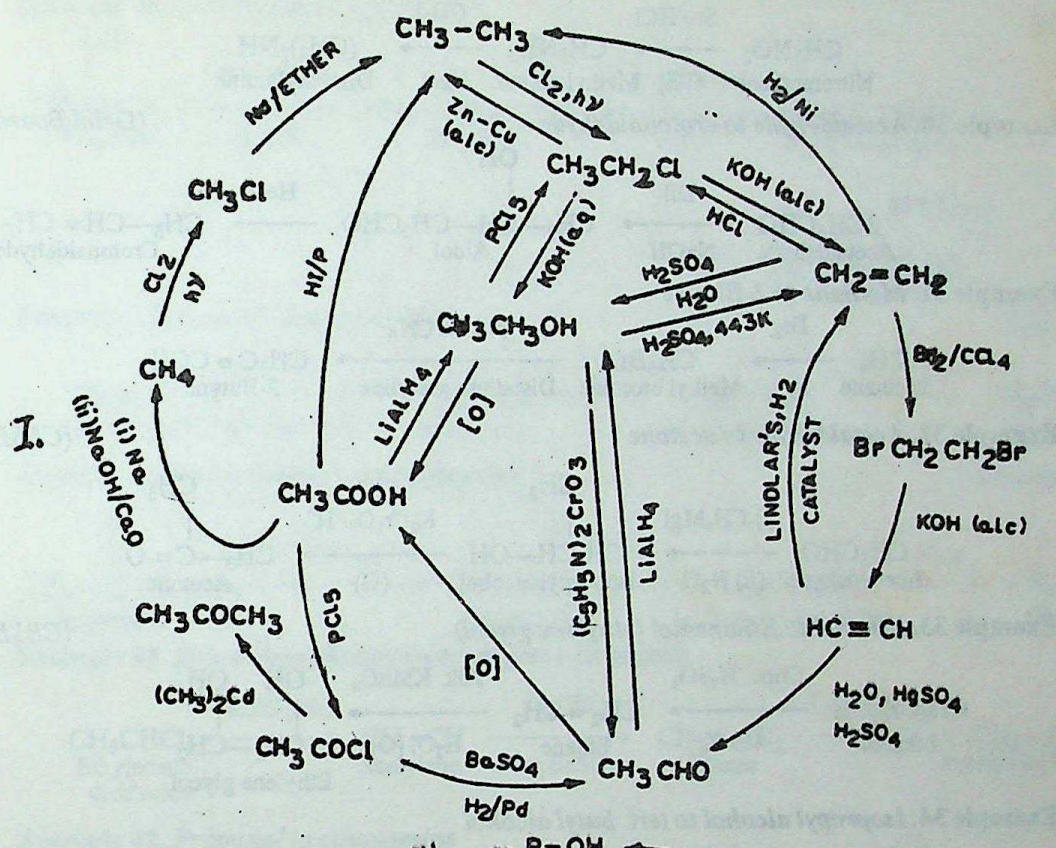
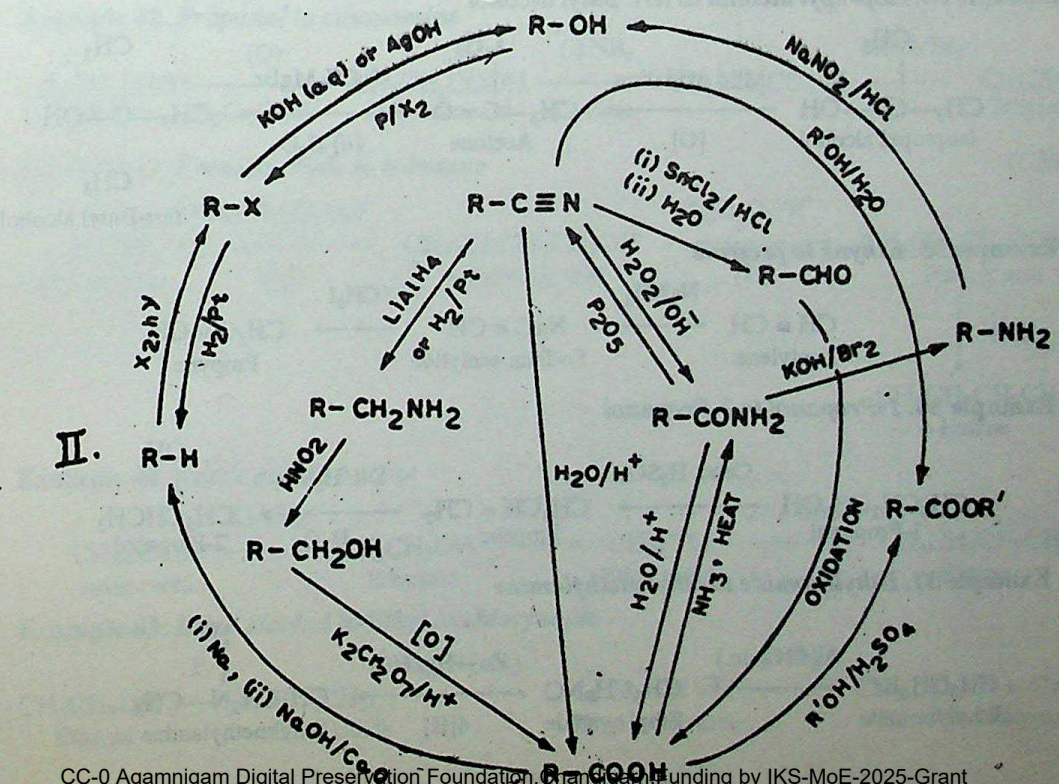
SOME IMPORTANT ROUTES FOR SOME ALIPHATIC CONVERSIONS





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Example 29. ***Nitromethane to dimethylamine*** *(CBSE 1990)*

$$\underset{\text{Nitromethane}}{CH_3NO_2} \xrightarrow[6[H]]{Sn/HCl} \underset{\text{Methyl amine}}{CH_3NH_2} \xrightarrow[\text{Heat}]{CH_3I} \underset{\text{Dimethylamine}}{(CH_3)_2NH}$$

Example 30. ***Acetaldehyde to crotonaldehyde*** *(Delhi Board 1993)*

$$\underset{\text{Acetaldehyde}}{2CH_3CHO} \xrightarrow[\text{NaOH}]{\text{Dil.}} \underset{\text{Aldol}}{CH_3-\overset{\overset{OH}{|}}{CH}-CH_2CHO} \xrightarrow{\text{Heat}} \underset{\text{Crotonaldehyde}}{CH_3-CH=CH-CHO}$$

Example 31. ***Methane to 2-Butyne***

$$\underset{\text{Methane}}{CH_4} \xrightarrow[h\nu]{Br_2} \underset{\text{Methyl bromide}}{CH_3Br} \xrightarrow[\text{Disodium acetylide}]{NaC\equiv CNa} \underset{\text{2-Butyne}}{CH_3C\equiv CCH_3}$$

Example 32. ***Acetaldehyde to acetone*** *(CBSE 1995)*

$$\underset{\text{Acetaldehyde}}{CH_3CHO} \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgI} \underset{\text{Isopropyl alcohol}}{CH_3\overset{\overset{CH_3}{|}}{CH}-OH} \xrightarrow[(O)]{K_2Cr_2O_7/H^+} \underset{\text{Acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O}$$

Example 33. ***Ethanol to Ethanediol (ethylene glycol)*** *(CBSE 1994)*

$$\underset{\text{Ethanol}}{CH_3CH_2OH} \xrightarrow[443\ K]{\text{Conc. } H_2SO_4} \underset{\text{Ethane}}{CH_2=CH_2} \xrightarrow[H_2O,\ [O]]{\text{Alk. } KMnO_4} \underset{\text{Ethylene glycol}}{\overset{\overset{OH}{|}}{CH_2}-\overset{\overset{OH}{|}}{CH_2}}$$

Example 34. ***Isopropyl alcohol to tert. butyl alcohol***

$$\underset{\text{Isopropyl alcohol}}{CH_3-\overset{\overset{CH_3}{|}}{CH}-OH} \xrightarrow[[O]]{\text{Mild oxidation}} \underset{\text{Acetone}}{CH_3-\overset{\overset{CH_3}{|}}{C}=O} \xrightarrow[(ii)\ H_2O]{(i)\ CH_3MgBr} \underset{\textit{tert}\text{-Butyl alcohol}}{CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH}$$

Example 35. ***Ethyne to propyne***

$$\underset{\text{Acetylene}}{CH\equiv CH} \xrightarrow{NaNH_2} \underset{\text{Sodium acetylide}}{NaC\equiv CH} \xrightarrow{CH_3I} \underset{\text{Propyne}}{CH_3C\equiv CH}$$

Example 36. ***1-Propanol to 2-Propanol***

$$\underset{\text{1-Propanol}}{CH_3CH_2CH_2OH} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{Propene}}{CH_3CH=CH_2} \xrightarrow[H_2O]{\text{Dil. } H_2SO_4} \underset{\text{2-Propanol}}{CH_3\overset{\overset{OH}{|}}{CH}CH_3}$$

Example 37. ***Ethylbromide to ethyl methylamine***

$$\underset{\text{Ethyl bromide}}{CH_3CH_2Br} \xrightarrow{AgCN\ (alc.)} \underset{\text{Ethyl cyanide}}{CH_3CH_2NC} \xrightarrow[4[H]]{Zn-Hg/HCl} \underset{\text{Ethylmethylamine}}{CH_3CH_2\overset{\overset{H}{|}}{N}-CH_3}$$

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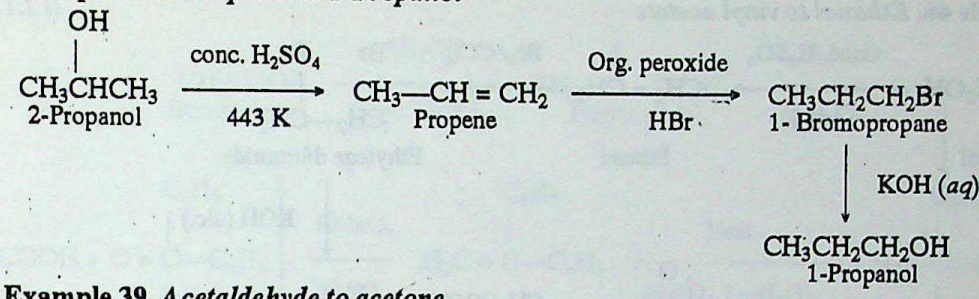
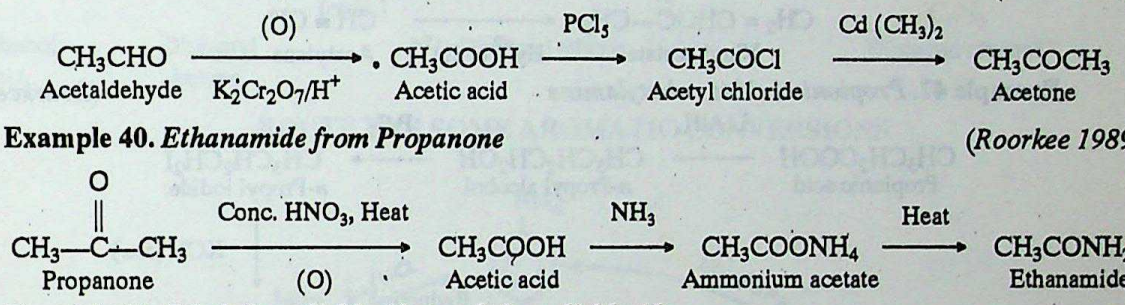
Some Examples of Aliphatic Conversions Involving THREE STEPS

Example 38. ***2-Propanol to 1-Propanol*** *(I.I.T. 1982)*

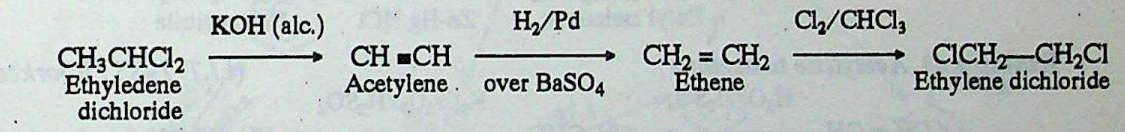


Example 39. ***Acetaldehyde to acetone*** *(CBSE 1992)*

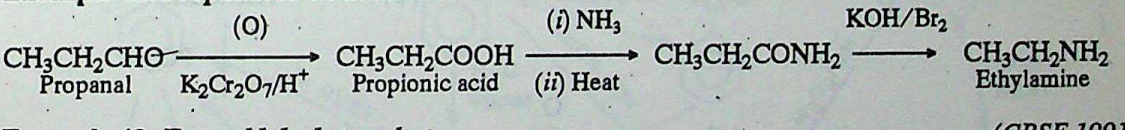


Example 40. ***Ethanamide from Propanone*** *(Roorkee 1989)*

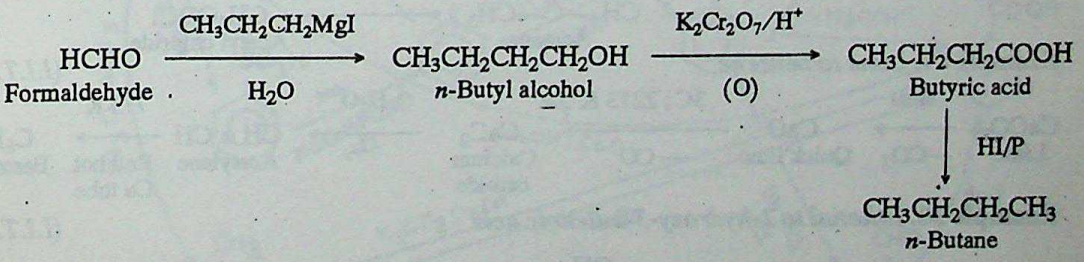
Example 41. ***Ethyledene dichloride to ethylene dichloride***



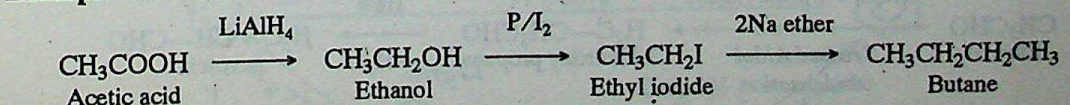
Example 42. ***Propanal to ethanamine***



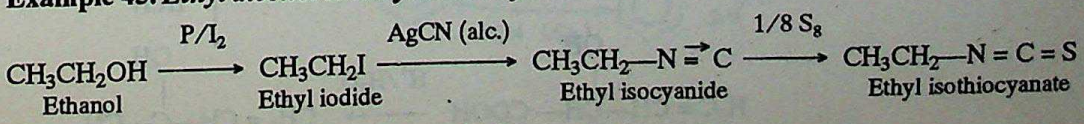
Example 43. ***Formaldehyde to n-butane*** *(CBSE 1991)*



Example 44. ***Acetic acid to butane***



Example 45. ***Ethyl alcohol to Ethyl isothiocyanate***



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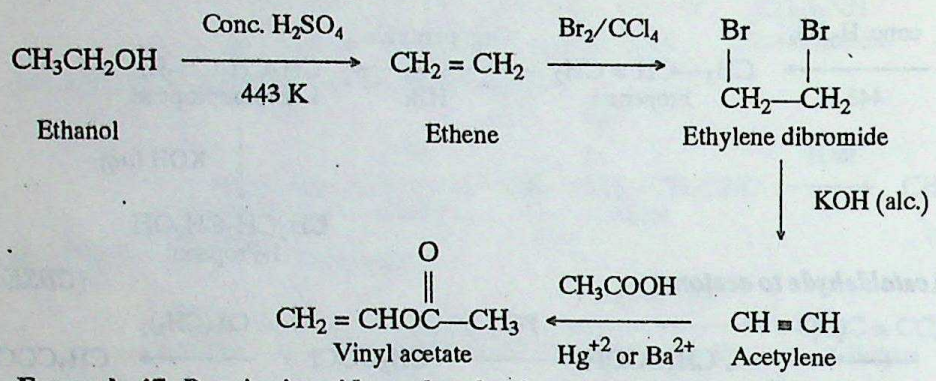
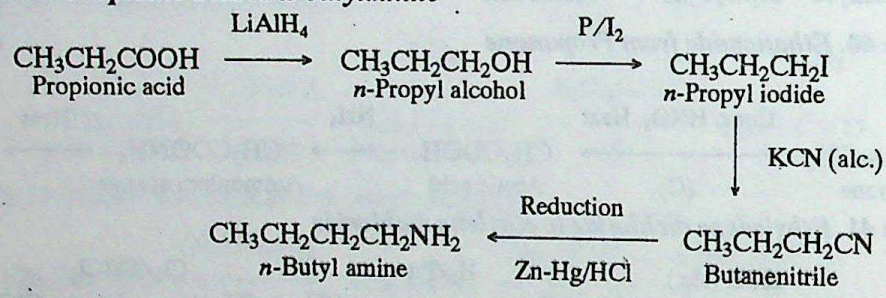
MULTISTEP ALIPHATIC CONVERSIONS

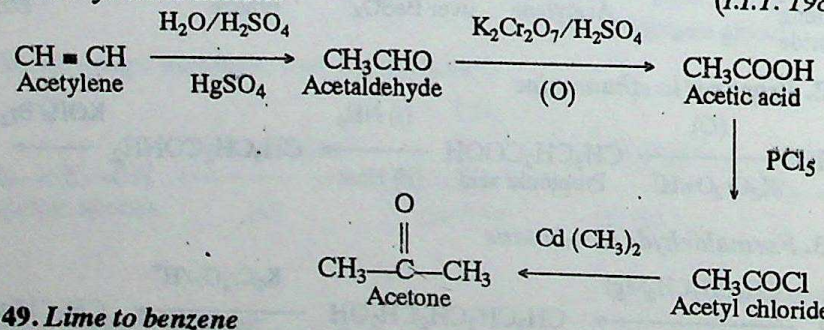
Example 46. ***Ethanol to vinyl acetate*** *(I.I.T. 1986)*



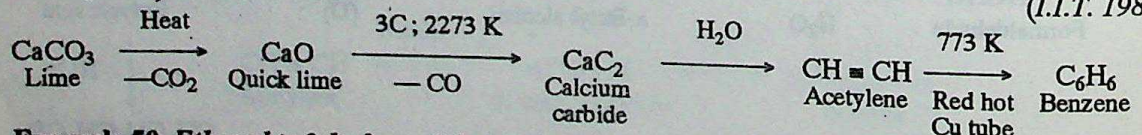
Example 47. ***Propionic acid to n-butylamine*** *(Roorkee 1985)*



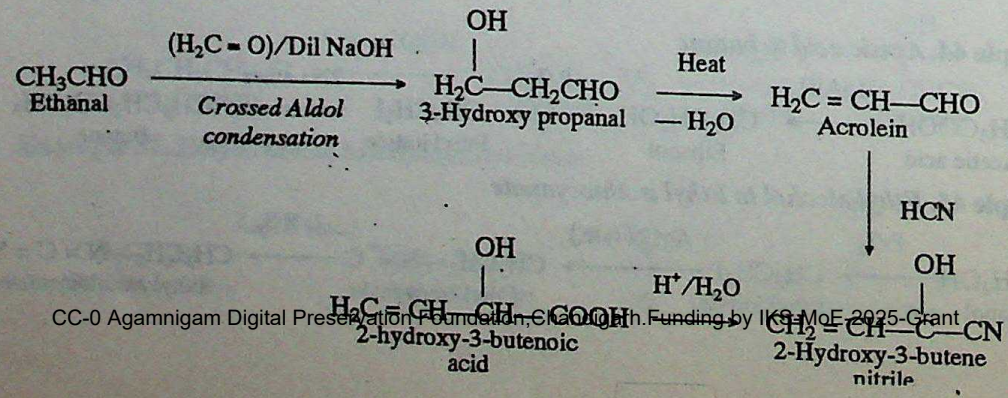
Example 48. ***Acetylene to acetone*** *(I.I.T. 1985 ; Roorkee 1986)*



Example 49. ***Lime to benzene*** *(I.I.T. 1987)*



Example 50. ***Ethanal to 2-hydroxy-3-butenoic acid*** *(I.I.T. 1990)*



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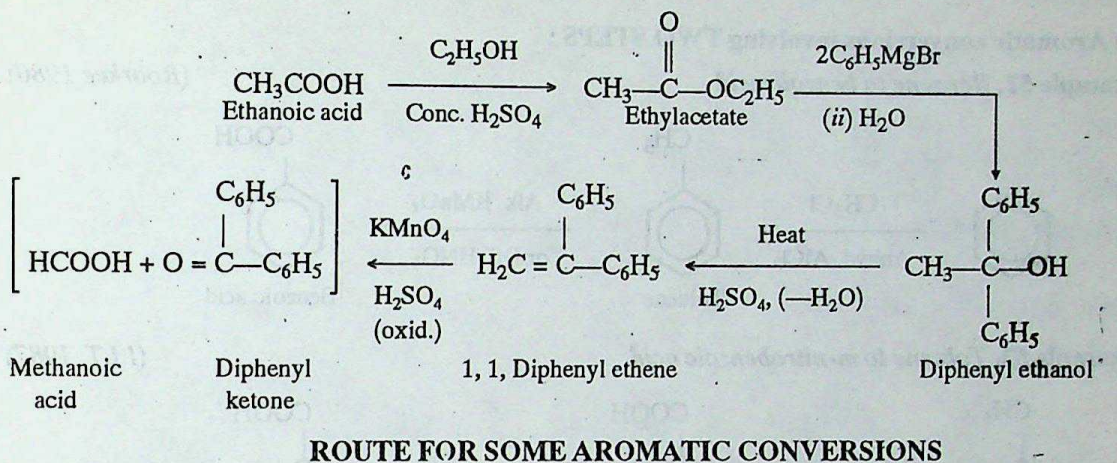
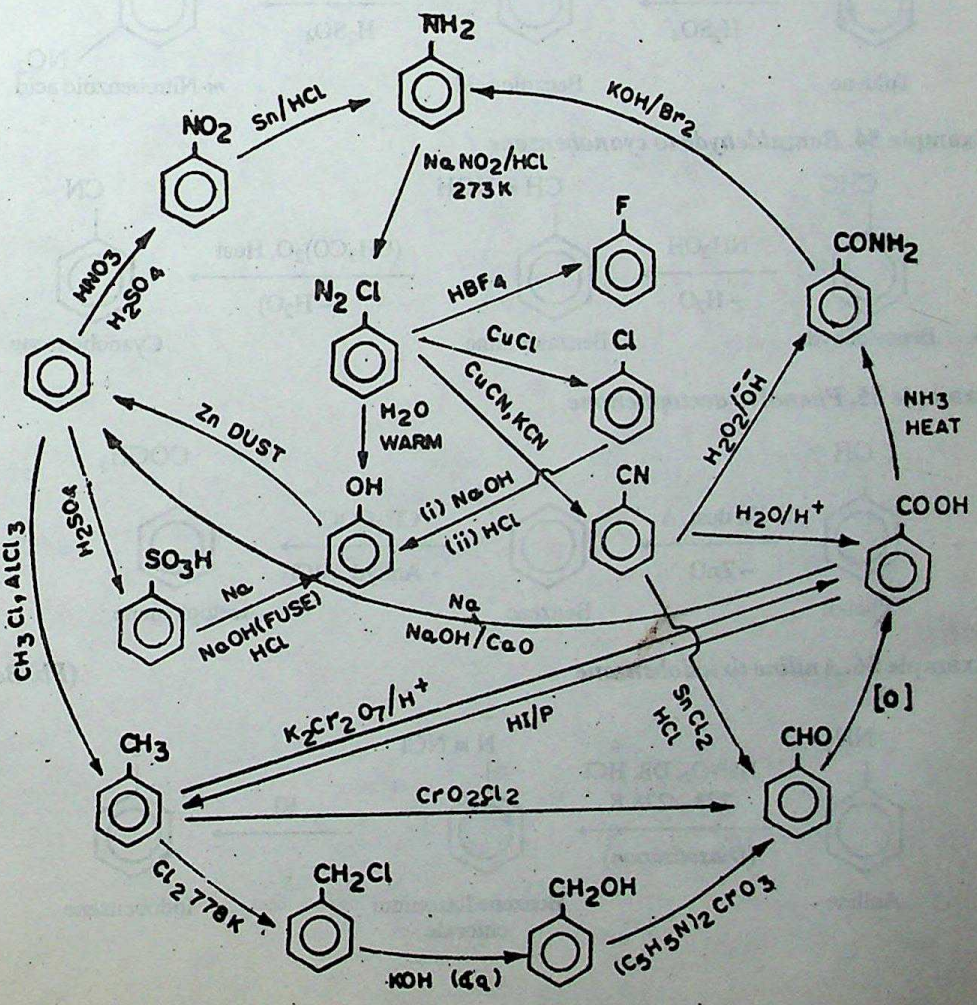
Example 51. *Ethanoic acid to a mixture of methanoic acid and diphenyl ketone.* (*I.I.T. 1991*)



ROUTE FOR SOME AROMATIC CONVERSIONS



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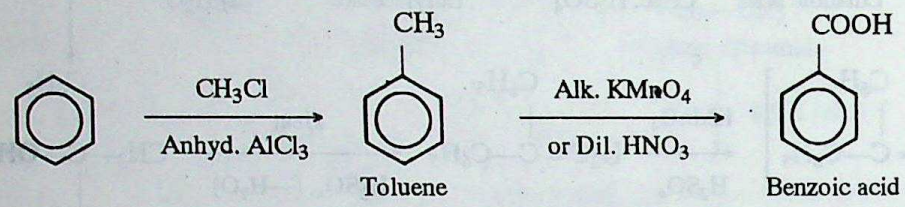
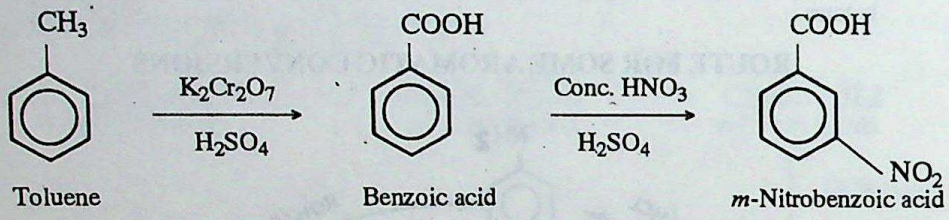
AROMATIC CONVERSIONS

(*a*) Aromatic conversions involving TWO STEPS :

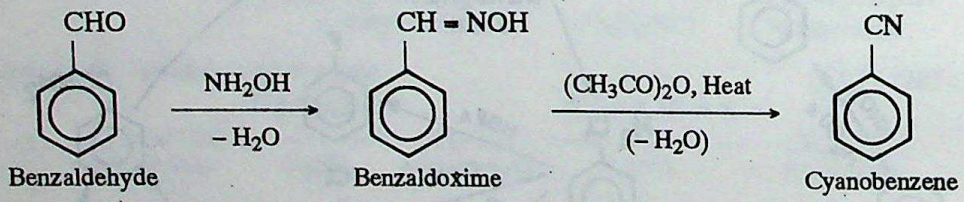
Example 52. ***Benzene to benzoic acid*** (*Roorkee 1980*)



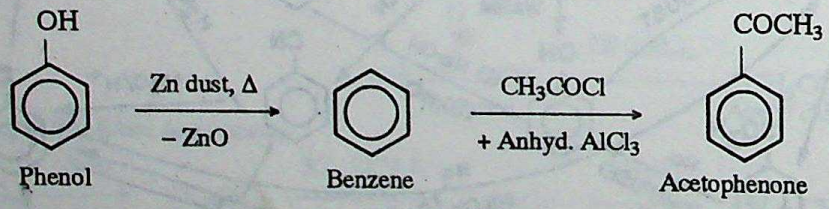
Example 53. ***Toluene to m-nitrobenzoic acid*** (*I.I.T. 1987*)



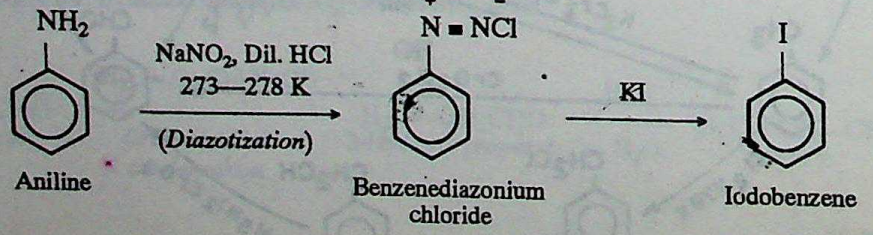
Example 54. ***Benzaldehyde to cyanobenzene*** (*I.I.T. 1988*)



Example 55. ***Phenol to acetophenone*** (*I.I.T. 1989*)



Example 56. ***Aniline to iodobenzene*** (*Pb. Board 1989 S*)



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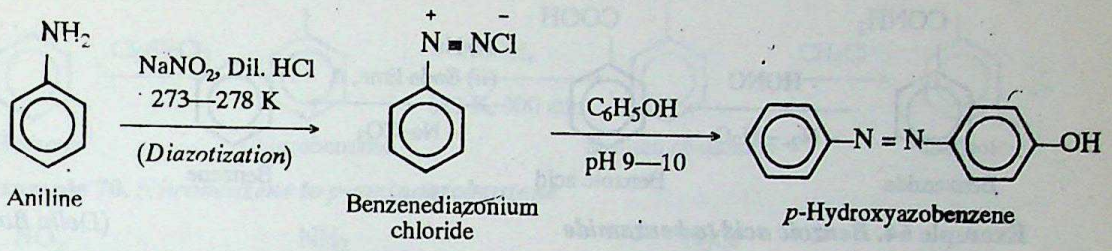
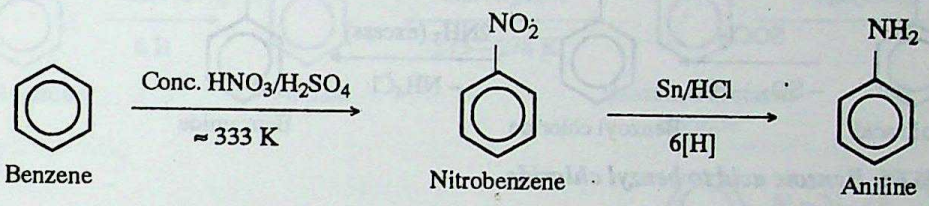
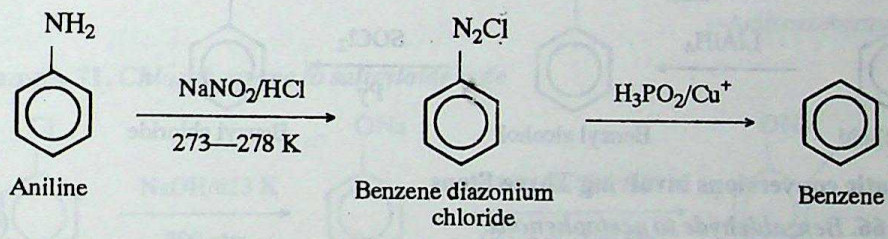
Example 57. ***Aniline to p-hydroxyazobenzene*** **(*Har. Board 1990*)**



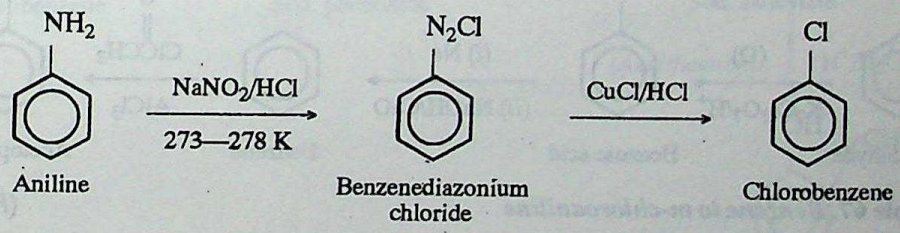
Example 58. ***Benzene to aniline*** **(*Delhi Board 1990 ; B.I.T. Ranchi 1990*)**



Example 59. ***Aniline to benzene***

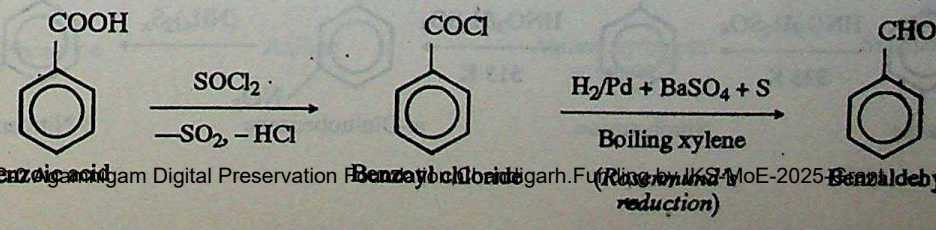


Example 60. ***Aniline to chlorobenzene*** **(*Delhi Board 1987 ; CBSE 1990 S, 94*)**



Example 61. ***Aniline to benzonitrile*** **(*CBSE 1991*)**

Example 62. ***Benzoic acid to benzaldehyde*** **(*CBSE 1991 S*)**



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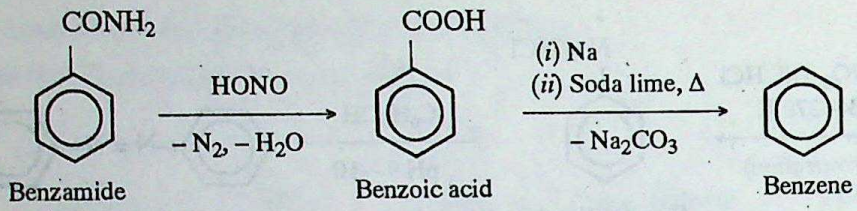
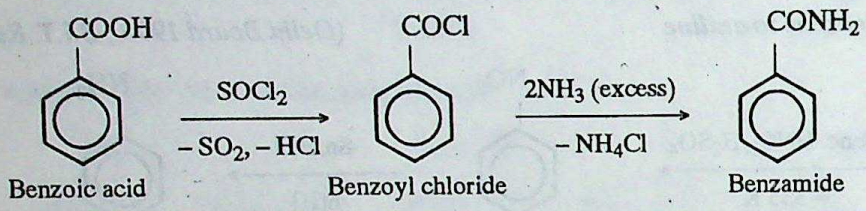
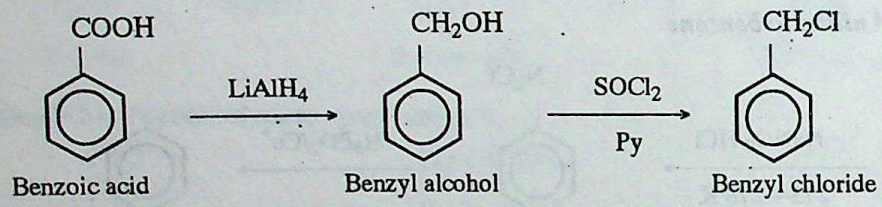
Example 63. ***Benzamide to benzene***



Example 64. ***Benzoic acid to benzamide*** (*Delhi Board 1992*)

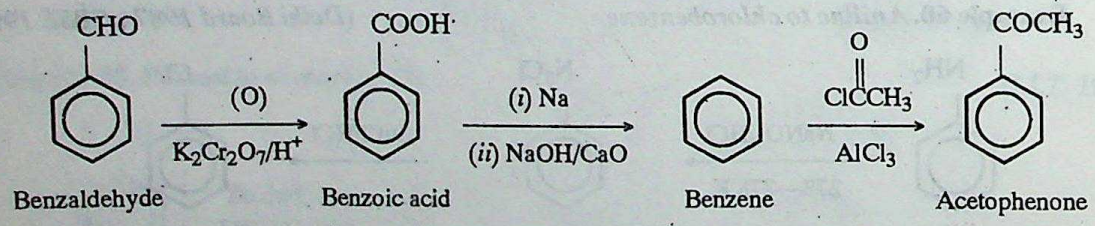


Example 65. ***Benzoic acid to benzyl chloride***

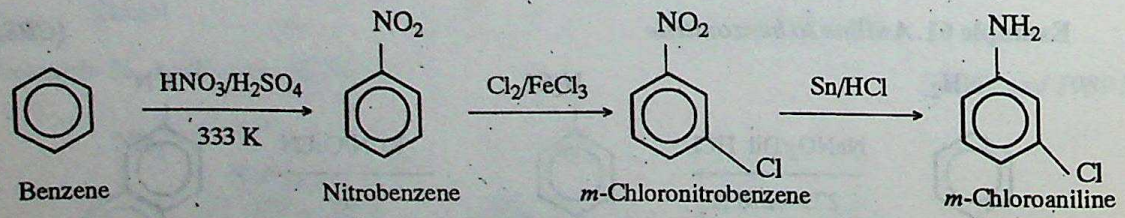


(*b*) Aromatic conversions involving Three Steps

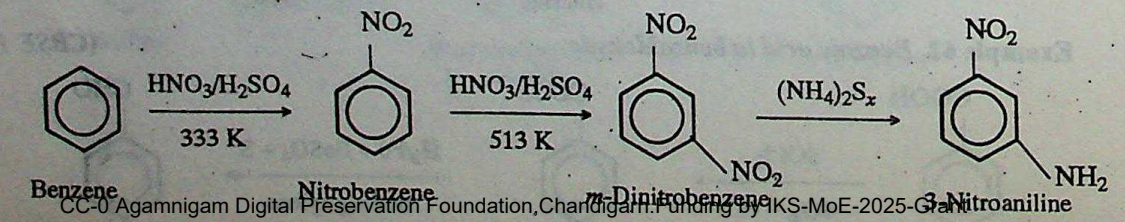
Example 66. ***Benzaldehyde to acetophenone*** (*CBSE 1995*)



Example 67. ***Benzene to m-chloroaniline*** (*Roorkee 1988*)



Example 68. ***Benzene to 3-nitroaniline***



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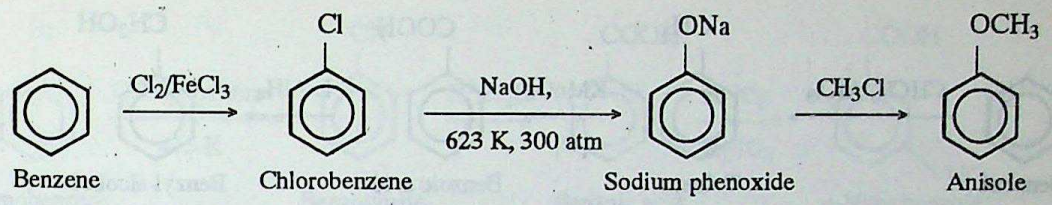
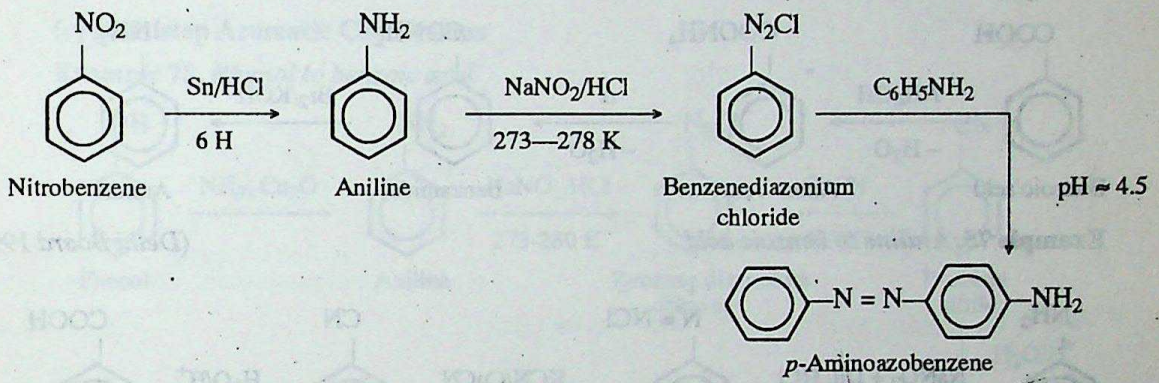
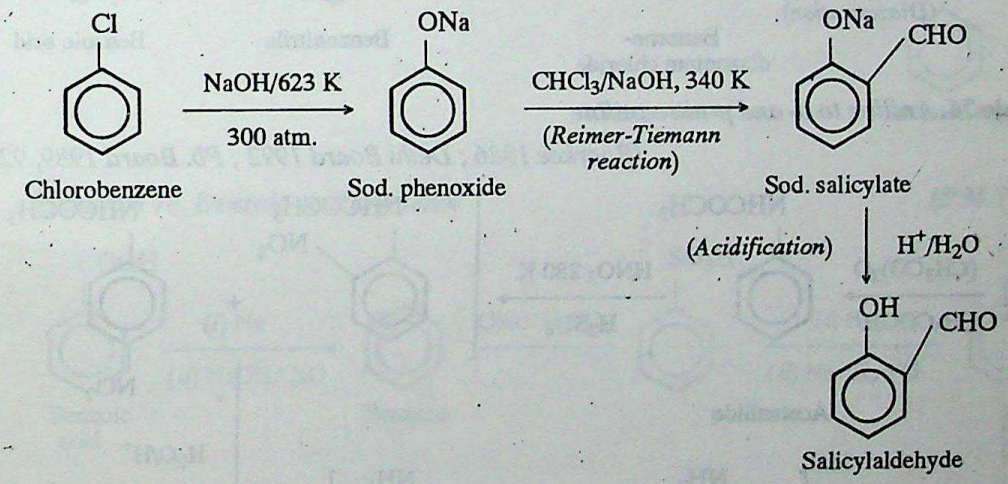
Example 69. ***Benzene to anisole***



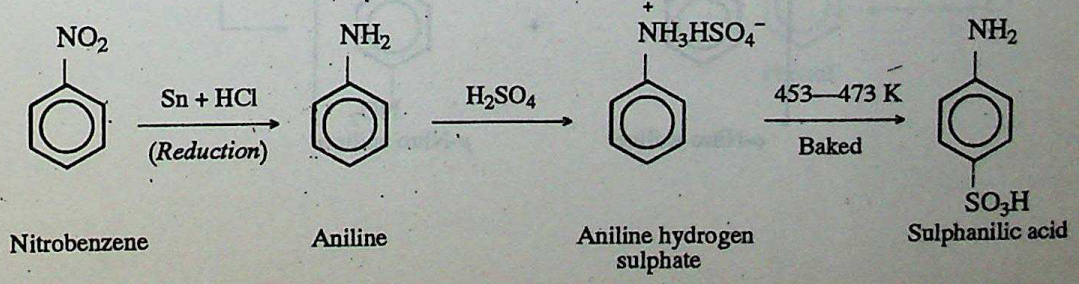
Example 70. ***Nitrobenzene to p-aminoazobenzene***



Example 71. ***Chlorobenzene to salicylaldehyde*** *(CBSE 1990)*



Example 72. ***Nitro benzene to sulphanilic acid*** *(Pb. Board 1993)*



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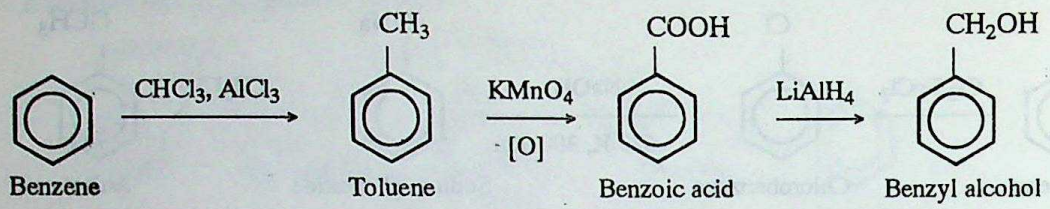
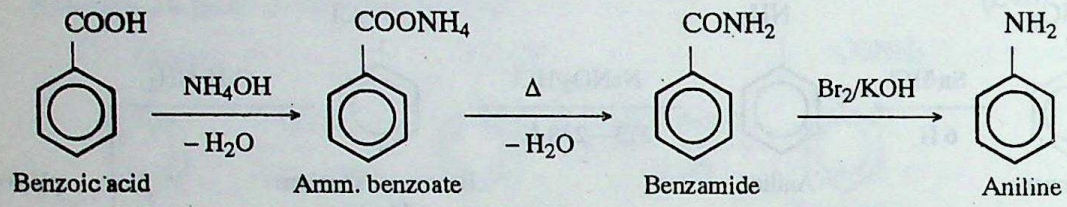
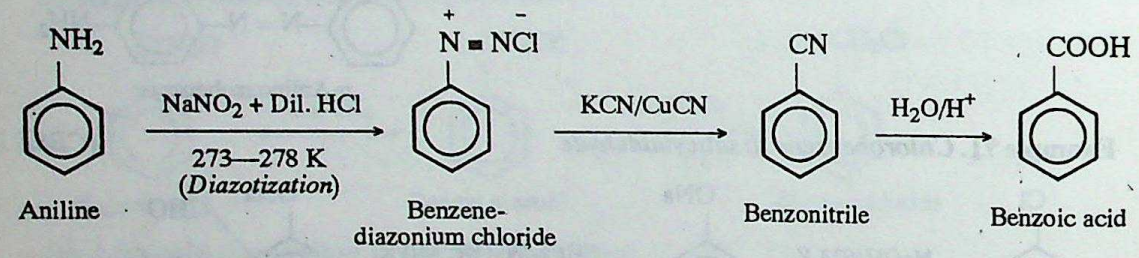
Example 73. ***Benzene to benzyl alcohol***



Example 74. ***Benzoic acid to aniline***

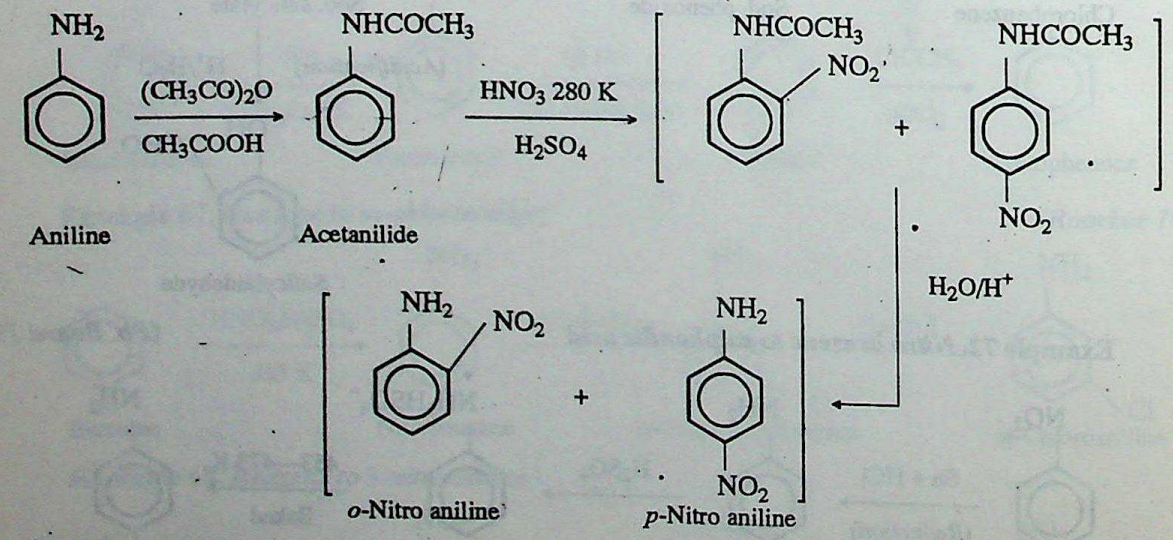


Example 75. ***Aniline to benzoic acid*** *(Delhi Board 1990)*



Example 76. ***Aniline to o- and p-nitroaniline***

(Roorkee 1986 ; Delhi Board 1992 ; Pb. Board 1989, 92, 93)



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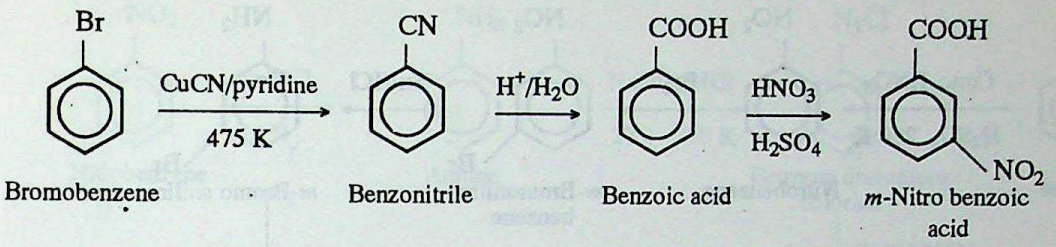
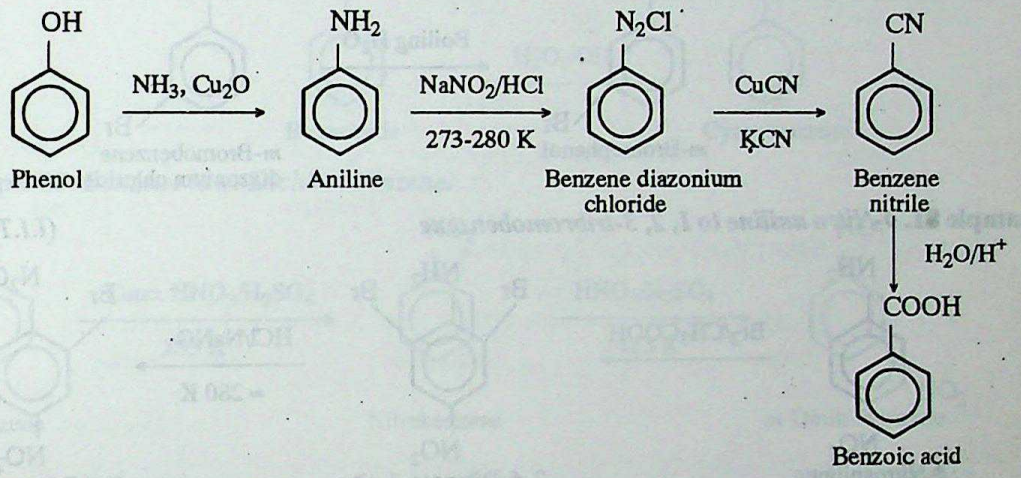
Example 77. ***Bromobenzene to m-nitrobenzoic acid*** *(M.L.N.R. Allahabad, 1994)*

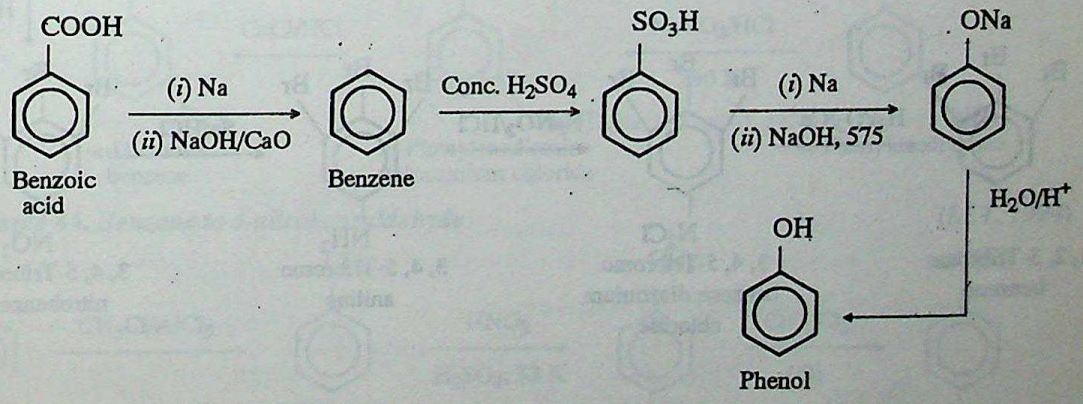


(*c*) Multistep Aromatic Conversions

Example 78. ***Phenol to benzoic acid***



Example 79. ***Benzoic acid to phenol*** *(P.M.T. Rohtak 1988)*



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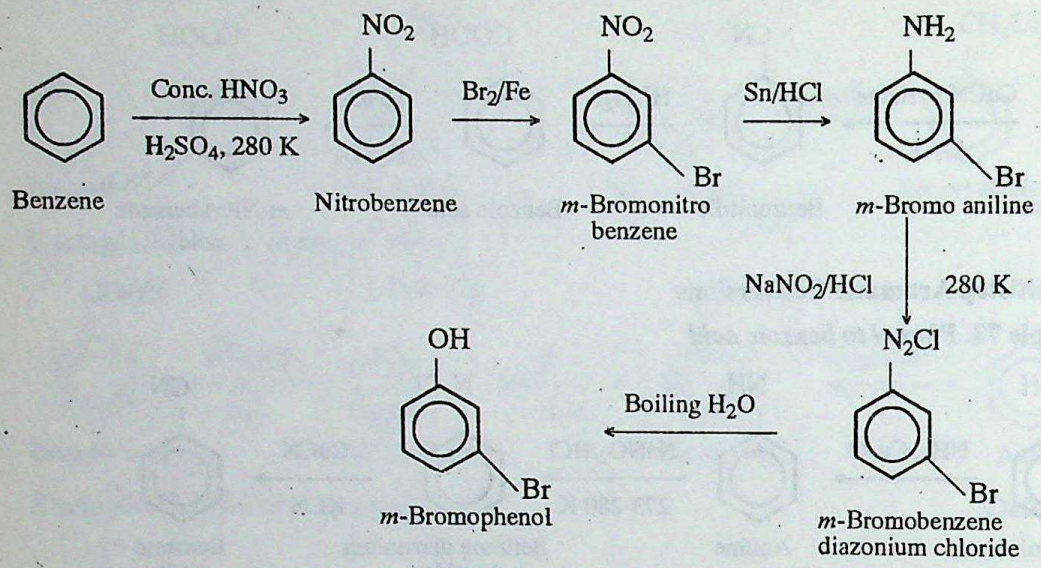
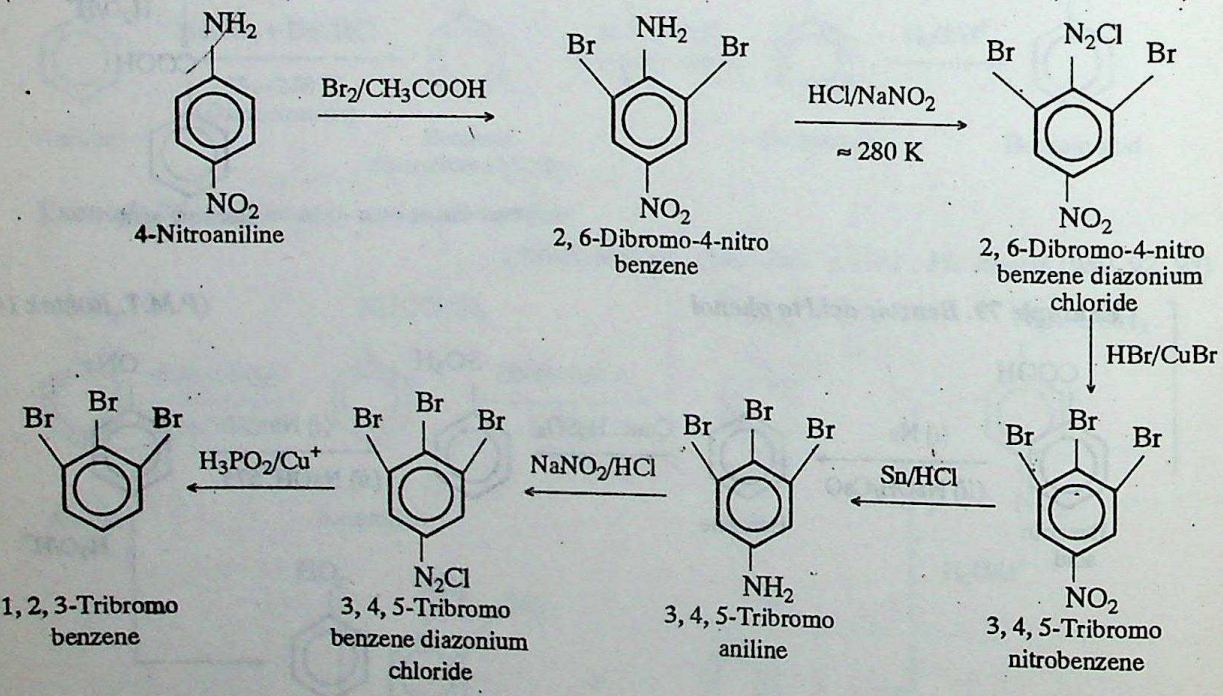
Example 80. ***Benzene to m-bromophenol***



Example 81. ***4-Nitro aniline to 1, 2, 3-tribromobenzene*** *(I.I.T. 1990)*



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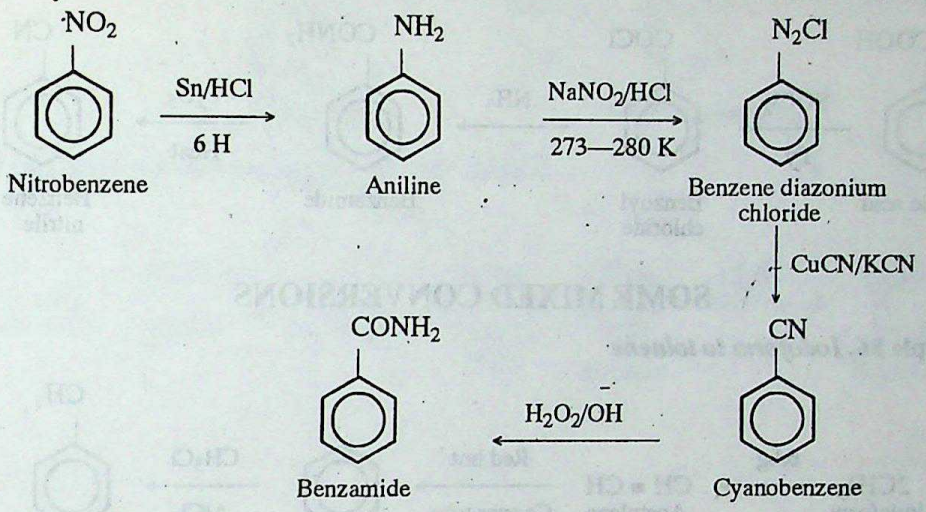
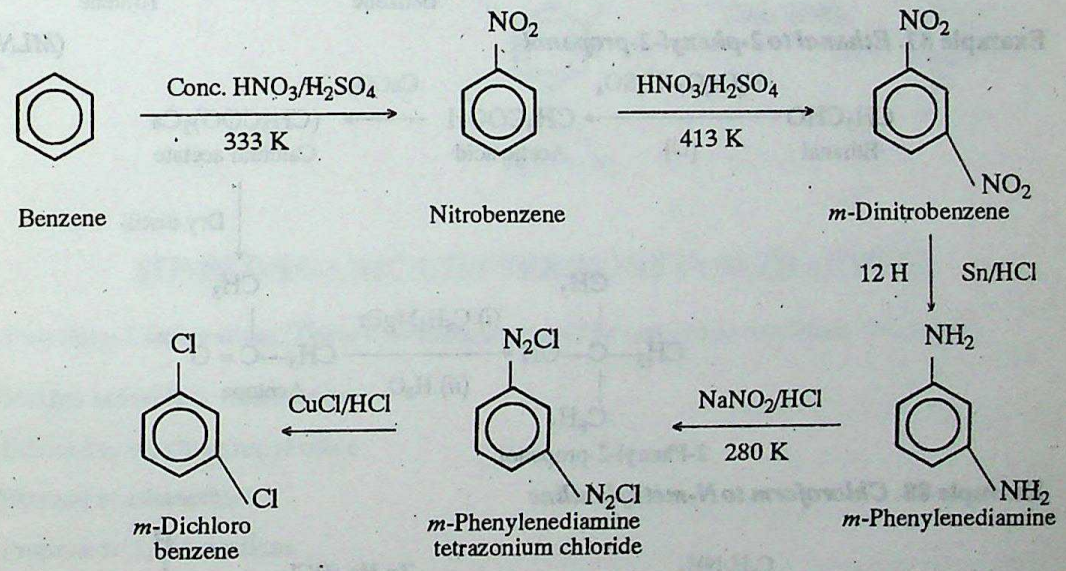
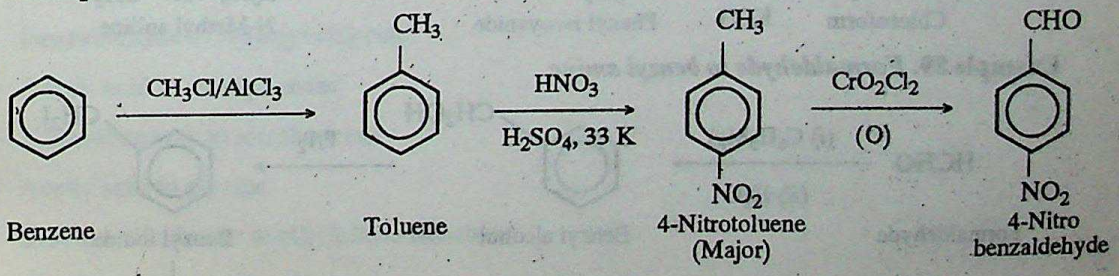
Example 82. ***Nitrobenzene to benzamide.*** *(I.I.T. 1994)*



Example 83. ***Benzene to m-Dichlorobenzene.***



Example 84. ***Benzene to 4 nitrobenzaldehyde*** *(I.I.T. 1994)*



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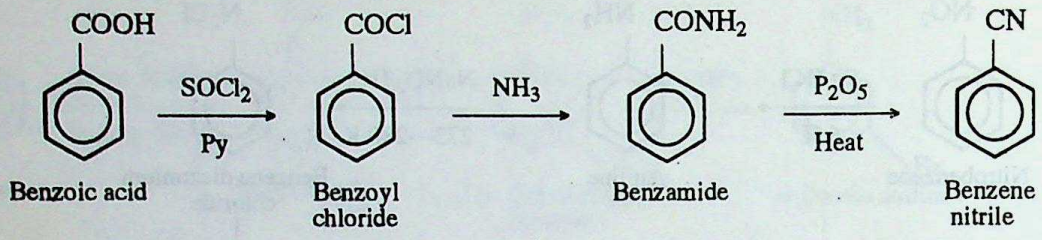
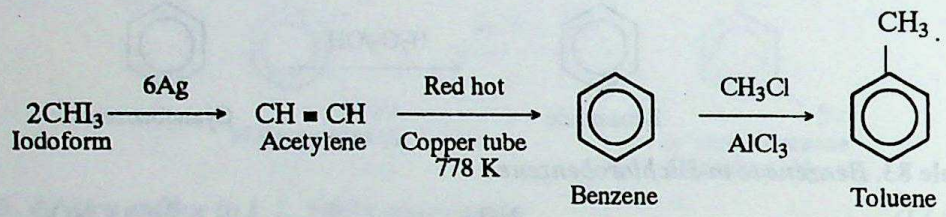
Example 85. ***Benzoic acid to benzene nitrile***

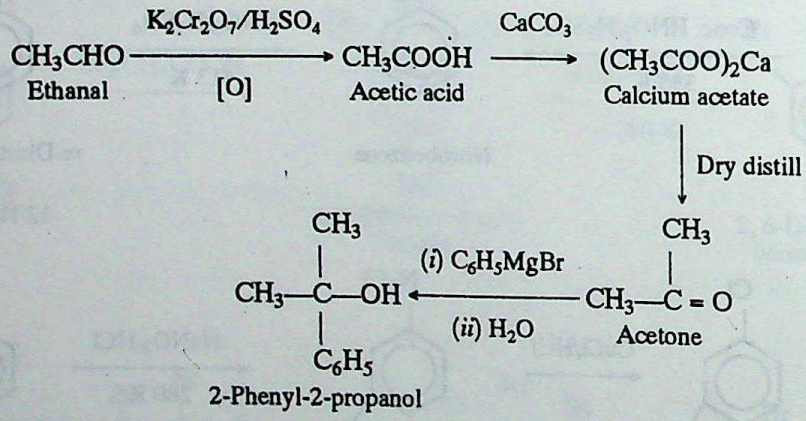


SOME MIXED CONVERSIONS

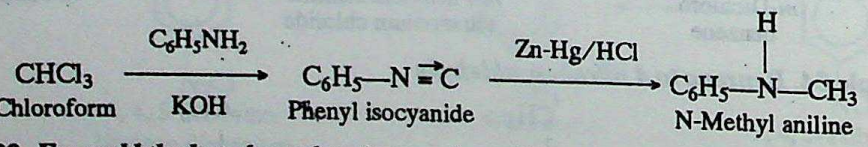
Example 86. ***Iodoform to toluene***



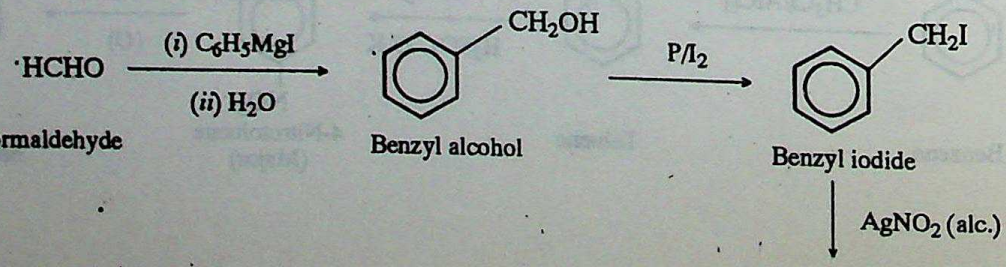
Example 87. ***Ethanal to 2-phenyl-2-propanol*** (*MLNR 1994*)



Example 88. ***Chloroform to N-methylaniline***



Example 89. ***Formaldehyde to benzyl amine***



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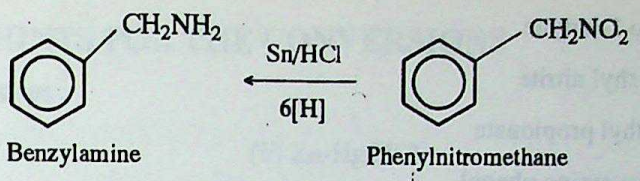
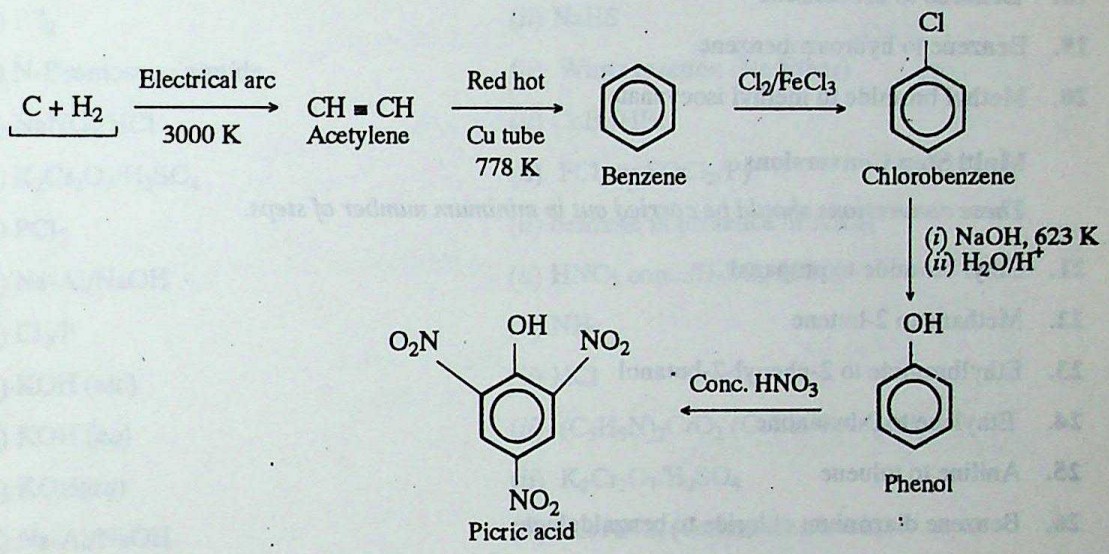


Example 90. ***Carbon and dihydrogen to picric acid***



SOME ORGANIC CONVERSIONS FOR PRACTICE

Two Step Conversions (*These conversions should be carried in maximum two steps.*)

1. Methyl bromide to ethanamine
2. Ethanol to ethylisopropyl ether
3. Ethanol to ethanethiol
4. Propene to 1, 5 hexadiene
5. Aniline to bromobenzene
6. Benzaldehyde to benzoyl chloride
7. Acetic acid to acetophenone
8. Chlorobenzene to nitrobenzene
9. Acetic acid to glycine
10. Ethylene dichloride to ethyledene chloride
11. Ethyl bromide to ethanal
12. Ethyl iodide to acetic acid
13. Chlorobenzene to benzaldehyde

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14. Acetylene to 1-butyne
15. Ethanol to ethyl nitrite
16. Ethene to ethyl propionate
17. Benzene to *p*-amino phenol
18. Benzene to azobenzene
19. Benzene to hydroazobenzene
20. Methyl bromide to methyl isocyanate

Multi Step Conversions

These conversions should be carried out in minimum number of steps.

21. Ethyl bromide to propanal
22. Methane to 2-butene
23. Ethylbromide to 2-phenyl-2-butanol
24. Ethylene to 2-butanone
25. Aniline to toluene
26. Benzene diazonium chloride to benzaldehyde
27. Benzene to 3, 3′-dinitrobiphenyl
28. Propionic acid to lactic acid
29. Acetic acid to pyruvic acid
30. Propionic acid to 1, 2-dibromopropionic acid
31. Acetic acid to melonic acid
32. Ethanal to 2-butenoic acid
33. Propyne to 2-methyl-2-propanol
34. Acetic acid to 2-butanol
35. Benzoic acid to benzenenitrile
36. Chlorobenzene to fluorobenzene
37. Benzene to 1, 3, 5-Trinitrobenzene
38. Aniline to salicylic acid
39. 2-Butanol to 2-nitroso-2-nitrobutane
40. 2-Propanol to isobutyric acid
41. Benzene to resorcinol.

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HINTS FOR THE CONVERSIONS

Carry out the following steps :

1. (*i*) $AgNO_2$ (alc.) (*ii*) Zn-Hg/HCl
2. (*i*) P/I_2 (*ii*) treatment with sodium isopropoxide
3. (*i*) P/I_2 (*ii*) NaHS
4. (*i*) N-Bromosuccinimide (*ii*) Wurtz reaction (Na/Ether)
5. (*i*) $NaNO_2$/HCl (*ii*) CuBr/HBr
6. (*i*) $K_2Cr_2O_7/H_2SO_4$ (*ii*) PCl_5 or $SOCl_2$/Py
7. (*i*) PCl_5 (*ii*) benzene in presence of $AlCl_3$
8. (*i*) Na-Al/NaOH (*ii*) HNO_3 conc./H_2SO_4 333 K
9. (*i*) Cl_2/P (*ii*) NH_3
10. (*i*) KOH (alc) (*ii*) HCl
11. (*i*) KOH (*aq*) (*ii*) $(C_5H_5N)_2CrO_3$ (Collin's reagent)
12. (*i*) KOH(*aq*) (*ii*) $K_2Cr_2O_7/H_2SO_4$
13. (*i*) Na-Al/NaOH (*ii*) $CO/AlCl_3$ (Gattermann koch)
    or (*i*) CH_3Cl/Na (*ii*) CrO_2Cl_2 (Etard's reaction)
14. (*i*) $NaNH_2$ (*ii*) C_2H_5I
15. (*i*) P/I_2 (*ii*) KNO_2
16. (*i*) HBr (*ii*) $AgOCOC_2H_5$
17. (*i*) HNO_3/H_2SO_4, 333 K (*ii*) Electrolysis in strongly acidic medium
18. (*i*) HNO_3/H_2SO_4, 333 K (*ii*) $LiAlH_4$
19. (*i*) HNO_3/H_2SO_4, 333 K (*ii*) Zn/NaOH
20. (*i*) AgCN (alc) (*ii*) HgO
21. (*i*) KCN (alc) (*ii*) $SnCl_2$/HCl
    (*iii*) H_2O/H^+ (hydrolysis)
22. (*i*) Br_2, *hv* (*ii*) $NaC \overset{+-}{\equiv} C\overset{-+}{Na}$
23. (*i*) KOH (aq) (*ii*) $K_2Cr_2O_7/H_2SO_4$
    (*iii*) PCl_5 (*iv*) $(C_2H_5)_2Cd$
    (*v*) C_6H_5MgBr (*vi*) H_2O (hydrolysis)
24. (*i*) HI (*ii*) KOH (*aq*)
    (*iii*) $K_2Cr_2O_7/H_2SO_4$ (*iv*) PCl_5
    (*v*) $(C_2H_5)_2Cd$

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25. (*i*) $NaNO_2/HCl$ (*ii*) H_3PO_2/Cu^+
(*iii*) $CH_3Cl/AlCl_3$

26. (*i*) H_3PO_2/Cu^+ (*ii*) $CO/AlCl_3$, (Gatterman Koch synthesis)

27. (*i*) HNO_3/H_2SO_4 (*ii*) $Cl_2/FeCl_3$
(*iii*) Na/dry ether

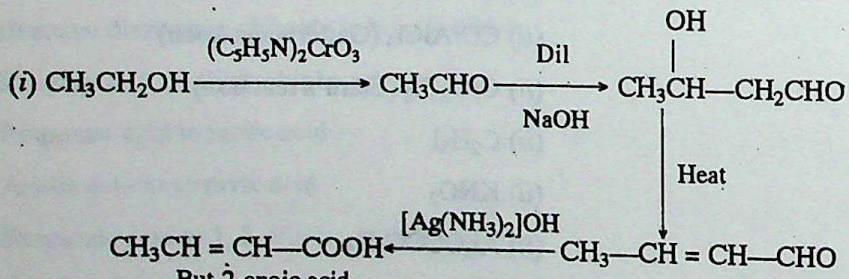
28. (*i*) Cl_2/P (HVZ) (*ii*) KOH (*aq*)
(*iii*) HCl (*aq*)

29. (*i*) PCl_5 (*ii*) KCN
(*iii*) H_2O/H^+
(*Pyruvic acid is 2-ketopropanoic acid*)

30. (*i*) Cl_2/P (HVZ) (*ii*) KOH (alc.)
(*iii*) Br_2/CCl_4

31. (*i*) Cl_2/P (HVZ) (*ii*) KCN (alc)
(*iii*) H_2O/H^+
(*Malonic acid is $CH_2(COOH)_2$*)

32.



33. (*i*) H_2O/H_2SO_4, $HgSO_4$ (*ii*) CH_3MgI (*iii*) H_2O

34. (*i*) PCl_5 (*ii*) $(C_2H_5)_2Cd$ (*iii*) $LiAlH_4$

35. (*i*) NH_3 (*ii*) Heat (*iii*) P_2O_5, Heat

36. (*i*) NH_3/Cu_2O, 475 K (*ii*) $NaNO_2/HCl$ (*iii*) HBF_4

37. (*i*) $Cl_2/FeCl_3$ (*ii*) NaOH, 623 K, 300 atm (*iii*) HCl
(*iv*) HNO_3 (conc.)/H_2SO_4 (*v*) Zn

38. (*i*) $NaNO_2/HCl$, 273 K (*ii*) H_2O/warm (*iii*) CCl_4, NaOH, 340
(*iv*) H_2O/H^+

39. (*i*) P/I_2 (*ii*) $AgNO_2$ (*iii*) $NaNO_2/HCl$

40. (*i*) P/I_2 (*ii*) KCN (alc) (*iii*) H_2O/H^+

41. (*i*) HNO_3/H_2SO_4, 333 K (*ii*) H_2SO_4/HNO_3, 413 K (*iii*) Sn/HCl
(*iv*) $NaNO_2/HCl$ (*v*) H_2O/warm.

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FILL IN THE BLANKS

Complete the following equations

1. $CH_3COOH \xrightarrow{NaOH} ? \xrightarrow[Heat]{NaOH/CaO} ?$

2. $(CH_3COO)_2Ca \xrightarrow{Heat} ?$

3. $CH_3COOH \xrightarrow{PCl_5} ? \xrightarrow{(C_2H_5)_2Cd} ?$

4. $CH_3COOH \xrightarrow{LiAlH_4} ? \xrightarrow{PBr_3} ? \xrightarrow{alc.\ KOH} ?$

5. $\begin{matrix} CH_3 \\ | \\ CH_3 \end{matrix} \xrightarrow{Cl_2} ? \xrightarrow{alc.\ KOH} ? \xrightarrow[(ii)\ HOH/Boil]{(i)\ H_2SO_4} ?$

6. $C_2H_5I \xrightarrow{AgCN} ?$

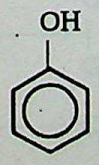
7. $CH_3COOH \xrightarrow{Br_2/P} ? \xrightarrow{KCN} ? \xrightarrow{dil.\ HCl} ?$

8. $HCHO \xrightarrow{NH_3} ?$

9. $CH_3COCH_3 \xrightarrow{CH_3MgBr} ? \xrightarrow{H_2O/H^+} ?$

10. $\begin{matrix} CH \\ ||| \\ CH \end{matrix} \xrightarrow[Hg^{2+}/H^+]{H_2O} ? \xrightarrow{Oxidation} ? \xrightarrow{Na} ? \xrightarrow{NaOH/CaO} ?$

13. $CH_3COOC_2H_5 \xrightarrow{NH_3} ? \xrightarrow{Br_2/KOH} ? \xrightarrow{HONO} ?$

11. 

$\xrightarrow{Br_2/H_2O} ?$

12.

$\xrightarrow[343\ K]{CHCl_3/NaOH} ?$

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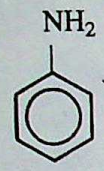
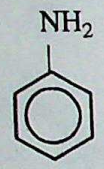
13. $CH_3CONH_2 \xrightarrow{Br_2/NaOH} ? \xrightarrow{CH_3COCl} ?$

14. 

$\xrightarrow[273-278\ K]{NaNO_2/HCl} ? \xrightarrow{Cu_2(CN)_2} ? \xrightarrow{dil.\ HCl} ?$

15. 

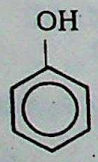
$\xrightarrow{Br_2\ (aq.)} ?$

17. $CH_3CH_2OH \xrightarrow{Cu/573\ K} ? \xrightarrow[\Delta]{NaOH}$

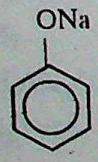
18. $(CH_3)_2NH \xrightarrow{HONO} ?$

19. $C_2H_5NH_2 \xrightarrow{HONO} ?$

20. $CH \equiv CH + H_2O \xrightarrow[1\%\ HgSO_4]{40\%\ H_2SO_4} ? \xrightarrow{HCN} ?$

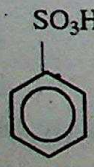
21. 

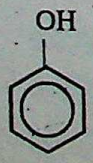
$\xrightarrow{HNO_3\ (Excess)} ?$

22. 

$\xrightarrow[Pressure]{CO_2/400\ K} ? \xrightarrow{H^+} ?$

23. $2\ CH_3\overset{O}{\overset{\|}{C}}CH_3 \xrightarrow{Base\ catalyst} ? \xrightarrow{Acid\ catalyst} ?$ *(I.I.T. 1988)*

24. 

$\xrightarrow{?}$ 

$\xrightarrow{CHCl_3/NaOH} ?$ *(I.I.T. 1988)*

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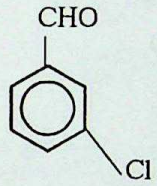
25. $\ldots\ldots \xrightarrow[\text{Heat}]{?} R{-}CONH_2 \xrightarrow{NaOH/Br_2} \ldots.$ *(I.I.T. 1990)*

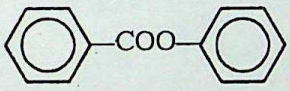
26. $CH_3CH = CHCHO \xrightarrow{NaBH_4} ? \xrightarrow{HCl/ZnCl_2} ? \xrightarrow{HCN/H^+} ?$ *(I.I.T. 1991)*

27. $C_6H_5COOH \xrightarrow{PCl_5} ? \xrightarrow{NH_3} ? \xrightarrow{P_2O_5} ? \xrightarrow{H_2/Ni} ?$ *(I.I.T. 1991)*

28. 

$\xrightarrow{50\%\ KOH} ?$ *(I.I.T. 1991)*

29. $C_6H_5CH_2{-}\underset{\underset{Br}{|}}{CH}{-}CH_3 \xrightarrow{\text{alcoholic KOH, }\Delta} ? \xrightarrow{HBr} ?$ *(I.I.T. 1993)*

30. 

$\xrightarrow[\text{Mononitration}]{HNO_3/H_2SO_4} ?$ *(I.I.T. 1993)*

31. $C_6H_5COOH + CH_3MgI \longrightarrow ? + ?$ *(I.I.T. 1993)*

ANSWERS

1. $\longrightarrow CH_3COONa \longrightarrow CH_4$

2. $\longrightarrow (CH_3)_2C = O$

3. $\longrightarrow CH_3COCl \longrightarrow CH_3COCH_2CH_3$

4. $\longrightarrow C_2H_5OH \longrightarrow C_2H_5Br \longrightarrow CH_2 = CH_2$

5. $\longrightarrow \underset{\underset{CH_2Cl}{|}}{CH_3} \longrightarrow \underset{\underset{CH_2}{\|}}{CH_2} \longrightarrow \underset{\underset{CH_2OH}{|}}{CH_3}$

6. $\longrightarrow C_2H_5NC$

7. $\underset{\underset{Br}{|}}{CH_2}COOH \longrightarrow \underset{\underset{CN}{|}}{CH_2}COOH \longrightarrow CH_2(COOH)_2$ Malonic acid

8. $\longrightarrow (CH_2)_6N_4$ Urotropine

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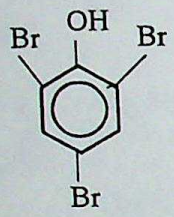
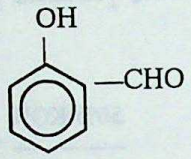
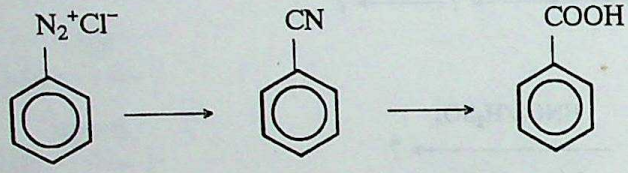
9. $\longrightarrow CH_3-C(CH_3)_2-OMgBr \longrightarrow CH_3-C(CH_3)_2-OH$

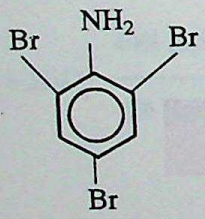
10. $\longrightarrow CH_3CHO \longrightarrow CH_3COOH \longrightarrow CH_3COONa \longrightarrow CH_4$

11. $\longrightarrow$ 

12. $\longrightarrow$ 

13. $\longrightarrow CH_3CONH_2 \longrightarrow CH_3NH_2 \longrightarrow CH_3OH$

14. $\longrightarrow$ 

15. $\longrightarrow$ 

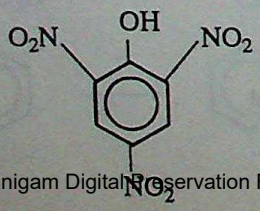
16. $\longrightarrow CH_3NH_2 \longrightarrow CH_3-NH-C(=O)-CH_3$

17. $\longrightarrow CH_3CHO \longrightarrow CH_3CH(OH)CH_2CHO$

18. $\longrightarrow (CH_3)_2N-NO$

19. $\longrightarrow C_2H_5OH$

20. $\longrightarrow CH_3CHO \longrightarrow CH_3CH(OH)(CN)$

21. $\longrightarrow$ 

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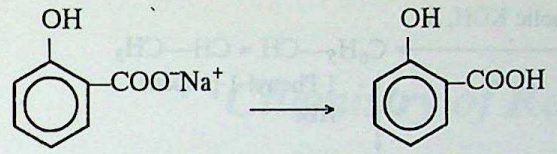
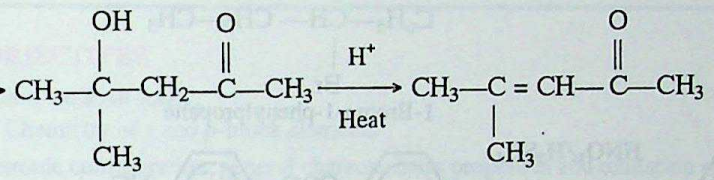
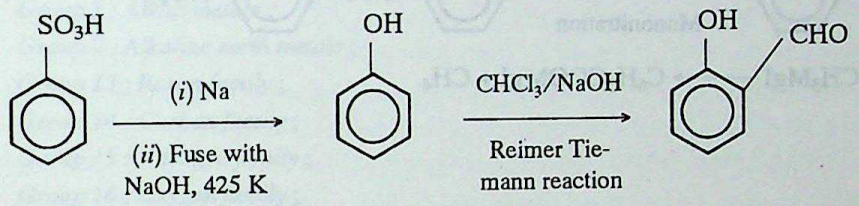
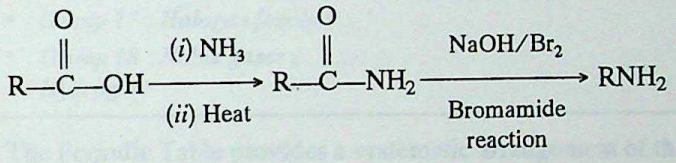
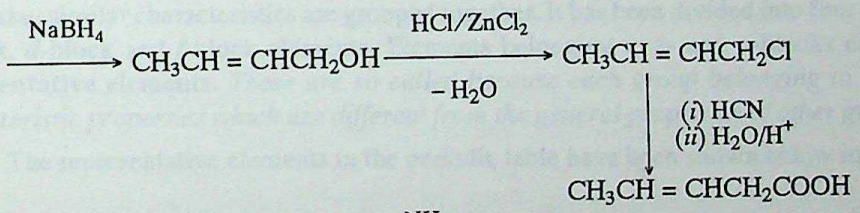
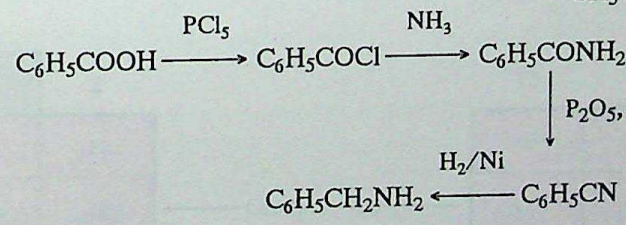
22. 

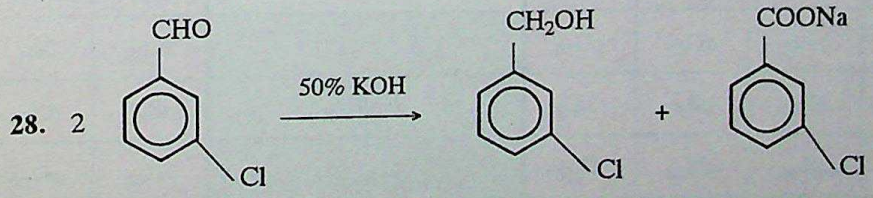
23. 

24. 

25. 

26. 

27. 

28. 

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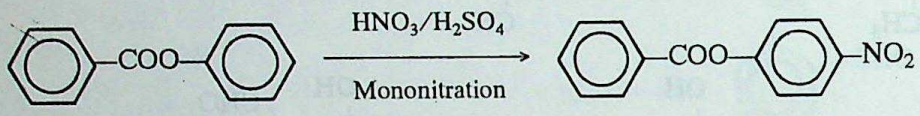
29. $C_6H_5—CH_2—CH(Br)—CH_3 \xrightarrow{\text{Alcoholic KOH, } \Delta} C_6H_5—CH = CH—CH_3$ (1-Phenyl-1-propene)

$\downarrow$ HBr

$C_6H_5—CH(Br)—CH_2—CH_3$ (1-Bromo-1-phenylpropane)

30. 

31. $C_6H_5COOH + CH_3MgI \longrightarrow C_6H_5COOMgI + CH_4$.

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10

Chemistry of Representative Elements

LEARNING OBJECTIVES

In this unit, we shall learn :

- The Chemistry of *s* and *p*-block elements
- Electronic configuration, general characteristics properties and oxidation state of the following :
- *Group 1 : Alkali metals* ;
- *Group 2 : Alkaline earth metals* ;
- *Group 13 : Boron family* ;
- *Group 14 ; Carbon family* ;
- *Group 15 : Nitrogen family* ;
- *Group 16 ; Oxygen family* ;
- *Group 17 : Halogen family* ;
- *Group 18 : Noble gases* ;
- *Hydrogen.*

The Periodic Table provides a systematic arrangement of the elements in such a manner that elements possessing similar characteristics are grouped together. It has been divided into four main blocks *viz.*, *s*-block, *p*-block, *d*-block and *f*-block elements. Elements belonging to *s*- and *p*-blocks of the table are known as **representative elements.** *These are so called because each group belonging to these blocks has its own characteristic properties which are different from the general properties of other groups.*

The representative elements in the periodic table have been shown below in tabular form :

1	2		13	14	15	16	17	18
$_{1}H$								$_{2}He$
$_{3}Li$	$_{4}Be$		$_{5}B$	$_{6}C$	$_{7}N$	$_{8}O$	$_{9}F$	$_{10}Ne$
$_{11}Na$	$_{12}Mg$	← Group 3—12 →	$_{13}Al$	$_{14}Si$	$_{15}P$	$_{16}S$	$_{17}Cl$	$_{18}Ar$
$_{19}K$	$_{20}Ca$		$_{31}Ga$	$_{32}Ge$	$_{33}As$	$_{34}Se$	$_{35}Br$	$_{36}Kr$
$_{37}Rb$	$_{38}Sr$	*d*-Block	$_{49}In$	$_{50}Sn$	$_{51}Sb$	$_{52}Te$	$_{53}I$	$_{54}Xe$
$_{55}Cs$	$_{56}Ba$		$_{81}Tl$	$_{82}Pb$	$_{83}Bi$	$*_{84}Po$	$*_{85}At$	$*_{86}Rn$
$*_{87}Fr$	$*_{88}Ra$							

|← *s*-Block →| |← *p*-Block →|

REPRESENTATIVE ELEMENTS

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The *s*- and *p*-block elements consist of groups 1, 2 and groups 13 to 18 of the Periodic Table. The *s*-block elements differ markedly from the *p*-block elements. This is illustrated by a few points of difference listed below :

(*i*) *s*-block elements predominantly form ionic compounds whereas the *p*-block elements exhibit a high degree of covalent character.

(*ii*) The *s*-block elements exhibit their highest oxidation state equal to the group number whereas the *p*-block elements exhibit their highest oxidation state equal to group number minus ten.

One of the characteristic feature regarding the oxidation states of *p*-block elements is that the lower oxidation state becomes more common with the increase in atomic number down the particular group. *This is because of the fact that they show gradual decrease in the tendency of the s-electrons of their valence shell to participate in bond formation, this effect is known as* **inert pair effect.**

(*iii*) The *s*-block elements act as good reducing agents whereas among the *p*-block elements the reducing character decreases and the oxidising character increases. For example, alkali metals (group 1) act as very good reducing agents whereas halogens (group 17) act as strong oxidising agents.

Apart from these variations among the *s*-block and *p*-block elements, it must be noted that the first member of each of these groups (belonging to either *s*- or *p*-block) differs markedly from the other heavier members of the group. This is mainly attributed to the following reasons :

(*a*) *The small size of first member* ;

(*b*) *The high electronegativity ; and*

(*c*) *The non-availability of d-orbitals for bonding among the first row elements (i.e. second period elements).*

It is observed that in many cases the first member of the group shows striking similarities with the second element of the neighbouring group on the right. Such a behaviour is known as **diagonal relationship.** In addition to it the elements of the first row, for example, C, N, O have the ability to form $p\pi$-$p\pi$ multiple bonds. This tendency diminishes for the subsequent row elements. However, the formation of multiple bonds by the heavier elements cannot be ruled out completely. Sufficient evidences are available which suggest the formation of multiple bonds by these elements in the compounds. This is ascribable to the $p\pi$—$d\pi$ bonding.

The chemistry of *s*- and *p*-block elements plays an important role in our daily life. For example, Na and K are of physiological importance in animals and plants. Besides, a number of important chemicals, *e.g.*, NaOH, HCl, H_2SO_4, fertilizers, $(C_2H_5)_4$ Pb (*antiknock*), etc. are derived from these elements.

Let us now discuss the chemistry of each of these groups separately to have a knowledge about their distinctive and characteristic features.

10.1. GROUP 1 ELEMENTS—The Alkali Metals

The elements *lithium* (Li), *sodium* (Na), *potassium* (K), *rubidium* (Rb), *caesium* (Cs) and *francium* (Fr), constitute group 1 of the periodic table. All these elements are metallic in nature and are called **alkali metals.** It is because their hydroxides are strong bases or alkalies. The last element of this group, francium, is radioactive and has a very short life span, therefore, very little is known about it. The alkali metals have one electron in the *s*-orbital of their valence shell. This indicates that these elements belong to *s*-block of the periodic table. The alkali metals show a marked similarity and gradation in their properties as discussed below. Their general electronic configuration may be represented as

$$[\text{Noble gas}]\ ns^1 \text{ ; where } n = 2 \text{ to } 7.$$

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The electronic configurations of alkali metals have been given in Table 10.1.

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Table 10.1. The Electronic Configuration of Alkali Metals

Element	*Symbol*	*Atomic number*	*Electronic Configuration*	*Abundance in earth's crust (ppm)*
Lithium	Li	3	[He] $2s^1$	65
Sodium	Na	11	[Ne] $3s^1$	28,300
Potassium	K	19	[Ar] $4s^1$	25,900
Rubidium	Rb	37	[Kr] $5s^1$	310
Caesium	Cs	55	[Xe] $6s^1$	7
Francium	Fr	87	[Rn] $7s^1$	—

General Trends in Physical Properties

All the alkali metals exhibit a striking resemblance in their physical and chemical properties. It is presumably because of their identical configuration (ns^1) in their valence shell. Some of the important physical constants of alkali metals are summarised in Table 10.2. The general variations among the physical properties of these elements are attributable to :

(*i*) the size of their atoms and ions ; and (*ii*) the low binding energy of the valence electron.

The trends observed in the variation of different physical properties are explained below :

1. Density. The densities of alkali metals are low and increase down the group. Potassium, however, is lighter than sodium.

Reason. *The low density of alkali metals is attributed to their large atomic size. However, in going down the group atomic size as well at atomic mass increases but the corresponding increases in atomic mass is not neutralised by the increase in atomic volume.* Thus, the ratio, *mass/volume, i.e.*, density gradually increases.

2. Melting Points and Boiling Points. All these metals have low melting points. The melting points decrease down the group.

Reason. *The low melting point are attributed to their larger atomic size, due to which the binding energies of their atoms in the crystal lattice are low. Further, in moving down the group, their atomic size increases and the strength of metallic bonds decreases which cause decrease in melting points.* The boiling points of the members of this group also follow the same order due to obvious reasons.

3. Atomic and Ionic Radii. The atoms of alkali metals have the largest size in their respective periods. The atomic radii increase on moving down the group among the alkali metals.

Table 10.2. Physical Properties of Group 1 Elements (Alkali Metals)

Element	*Atomic mass*	*Atomic radius*[a] *(pm)*	*Ionic radius*[b] *(pm)*	*Ionization energy (kJ mol^{-1})* *I*	*II*	*Electro-negativity*[c]	*Density*[d] *(g cm^{-3})*	*Melting point (K)*	*Boiling point (K)*	*E° (volts)*[e] *$M^+(aq) + e^- \longrightarrow M(s)$*
Lithium	6.94	152	76	520	7298	0.98	0.35	453.5	1620	– 3.03
Sodium	22.99	186	102	496	3562	0.93	0.97	370.8	1154.4	– 2.71
Potassium	39.10	227	138	419	3051	0.82	0.86	336.2	1038.5	– 2.93
Rubidium	85.47	248	152	403	2633	0.82	1.53	312.0	961.0	– 2.99
Caesium	132.91	265	167	376	2230	0.79	1.90	301.5	978.0	– 3.02
Francium[f]	223	375[g]	—	—	—	—	—	—	—	—

(*a*) Metallic radius (co-ordination number = 8) ; (*b*) Values are for co-ordination number 6 ;
(*c*) Pauling scale ; (*d*) 293 K ; (*e*) 298 K ; (*f*) Radioactive ; (*g*) Approximate value.

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Reason. *On moving down the group, there is a progressive addition of new energy shells. Although, the nuclear charge also increases down the group but the effect of addition of new shells in more predominant.*

Alkali metals change into positively charged ions by losing their lone valence electron. The radii of positive ion is smaller as compared to that of parent atom. Within the group, the ionic radii increase with increase in atomic number.

The alkali metal ions get extensively hydrated in aqueous solutions. Smaller is the size of ion more is the extent or degree of hydration. Thus, as a matter of fact the ionic radii in water decrease from Li^+ to Cs^+ *i.e.* the ion which should have been the smallest is actually the largest in size in water. Thus, the **ionic radii in aqueous solutions** follows the order

$$Li^+ > Na^+ > K^+ > Rb^+ > Cs^+$$

For the sake of comparison the ionic radii in gaseous state and those in aqueous state are being given below :

	Ionic Radius (pm)	*Ionic Radius of Hydrated ion (pm)*	*ΔH Hydration (kJ mol^{-1})*
Li^+	60	340	– 519
Na^+	95	276	– 406
K^+	133	232	– 322
Rb^+	148	228	– 293
Cs^+	169	228	– 264
	INCREASE ↓	DECREASE ↓	DECREASE ↓

4. Ionisation Energy and Electropositive Character. The first ionisation energies of alkali metals are quite low as compared with the elements of the other groups belonging to the same period. However, within the group, the ionisation energies of the alkali metals decrease down the group.

Reason. *The atoms of alkali metals are the largest in their respective periods, therefore, the outer most electrons which are far away from the nucleus experience a less force of attraction with the nucleus and hence can be easily removed.*

Decrease in ionisation energy on moving down the group is due to increase in size of the atoms of alkali metals and increase in the magnitude of screening effect by virtue of increase in number of intervening electrons.

On account of their low ionisation energies, these metals have a strong tendency to lose their valence electrons and thus change into positive ions. Consequently, **alkali metals are strongly electropositive or metallic in character.** As this tendency for losing electrons increases down the group, the electropositive character increases.

5. Oxidation State. The alkali metals have a strong tendency to lose their valence electron and change into unipositive ions. Thus, alkali metals exhibit + 1 oxidation state in their compounds.

$$\underset{[\text{Noble gas}]\ ns^1}{M} \longrightarrow \underset{[\text{Noble gas}]}{M^+} + e^-$$

$$\underset{[Ne]\ 3s^1}{Na} \longrightarrow \underset{[Ne]}{Na^+} + e^-$$

Reason. *By loss of solitary valence electron, these metals acquire the stable configuration of a noble gas, therefore these have no tendency to form the M^{2+} ions in any of their compounds. The magnitude*

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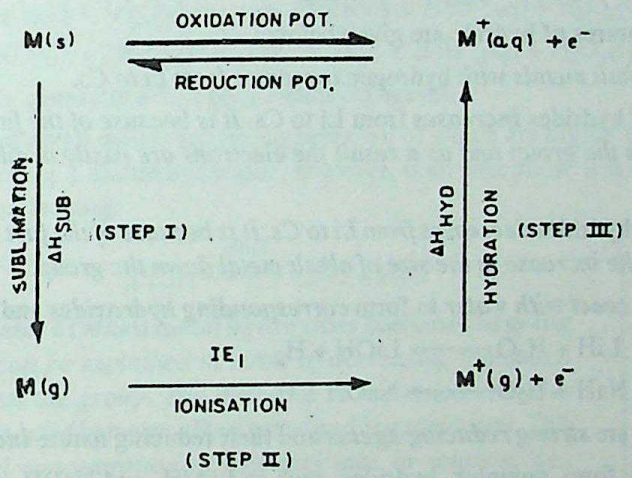
of second ionisation energy is very high and is not available under the conditions of formation of chemical bonds.

6. Reducing Properties. The tendency of an element to lose electron is compared by the values of reduction potential. A look at the values, listed in Table 10.2, reveals that alkali metals have low values of reduction potential and therefore have a strong tendency to lose electrons and act as good reducing agents. The reducing character increases from sodium to caesium. However lithium is the strongest reducing agent among all the alkali metals inspite of its highest I.E.

Reason. *Due to low ionisation energy the alkali metals have a strong tendency to lose their valence electron easily and thus, act as good reducing agents. The reducing character increases from Na to Cs because the ionisation energy decreases in that order. However, Li exhibits an anomalous value inspite of its highest ionisation energy. This is because the determination of reduction (or oxidation) potential involves the following sequence of steps.*



The overall tendency for the change depends on net effect of the three steps. Now since Li^+ ion is the smallest in size, therefore, the large amount of energy released in step III (heat of hydration) compensates for the higher ionisation energy and hence explains the low value of reduction potential of lithium and its strongest reducing character.

8. Flame Colouration. All the elements impart characteristic colour to Bunsen flame as described below :

Li	Na	K	Rb	Cs
Red	Golden yellow	Pale violet	Violet	Blue

Reason. *When energy is supplied to these elements in their salts, especially chlorides (due to more volatile character) the electron in their valence shells get excited to higher energy states. When these electrons jump back to their ground states they emu energy in the form of radiations which falls in the visible region, imparting a characteristic colouration to the flame.*

9. Photoelectric effect. Alkali metals (except Li) exhibit photoelectric effect. (A phenomenon of emission of electrons from metal surface by exposing it to visible light).

Reason. *The ability to exhibit photoelectric effect is attributed to low values of their ionisation energies. Lithium does not emit photoelectrons when exposed to light due to high IE value.*

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Chemical Properties

The alkali metals are highly reactive elements. The cause for their high chemical reactivity is :

(*a*) *low value of first ionisation energy ; and*

(*b*) *low heat of atomisation.*

As the value of ionisation energy decreases down the group from lithium to caesium therefore **the reactivity of alkali metals increases from Li to Cs.** These elements are highly reactive especially towards the more electronegative elements such as chlorine and oxygen. The important chemical characteristics of alkali metals are being discussed as follows :

1. Hydrides. Alkali metals react with dry hydrogen to form crystalline hydrides which are ionic in nature.

$$2M + H_2 \xrightarrow{\text{Heat}} 2\overset{+}{M}\overset{-}{H}$$

Some important features of hydride are given below :

(*i*) ***Reactivity of alkali metals with*** hydrogen ***increases from Li to Cs.***

(*ii*) ***Ionic nature*** of hydrides ***increases*** from Li to Cs. *It is because of the fact, that ionisation energy decreases down the group and as a result the electrons are easily available to H for forming H^- ion.*

(*iii*) The ***stability*** of hydrides ***decreases from Li to Cs. It is because of the fact that M—H bond becomes weaker due to the increase in the size of alkali metal down the group.***

(*iv*) These hydrides ***react with water*** to form ***corresponding hydroxides*** and hydrogen gas

$$LiH + H_2O \longrightarrow LiOH + H_2$$

$$NaH + H_2O \longrightarrow NaOH + H_2.$$

(*v*) These hydrides are ***strong reducing agents*** and their reducing nature ***increases down the group.***

Alkali metals also form complex hydrides such as $LiAlH_4$ and $NaBH_4$, which are good reducing agents.

2. Oxides and Hydroxides. Alkali metals when burnt in air form different kinds of oxides. For example, the alkali metals on reaction with limited quantity of oxygen form normal oxides of the formula, M_2O.

$$2M + \frac{1}{2}O_2 \longrightarrow M_2O$$

(where M = Li, Na, K, Rb, Cs).

However, when heated with excess of air, lithium forms *normal oxide,* Li_2O, sodium forms *peroxide,* Na_2O_2, whereas potassium, rubidium and caesium form *superoxides* having general formula MO_2.

$$2Li + \frac{1}{2}O_2 \longrightarrow \underset{\text{Lithium oxide}}{Li_2O}$$

$$2Na + O_2 \longrightarrow \underset{\text{Sodium peroxide}}{Na_2O_2}$$

$$K + O_2 \longrightarrow \underset{\text{Potassium superoxide}}{KO_2}$$

Reason. ***The simple fact that explains the stability and formation of these oxides is that, the cation with strong electrical field around it is stabilised by the anion with strong field and cation with weak field is stabilised by anion with weak field. The size of Li^+ ion is smaller and therefore, it has a strong***

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positive field around it. Thus, *it can stabilise a relatively small anion (O^{2-}) with strong negative field around it leading to the formation of Li_2O. On the other hand, Na^+ ion being a larger cation, has a weak positive field around it and can stabilise a bigger anion i.e., the one with a weak negative field around it like O_2^{2-} ion forming Na_2O_2.*

Similarly, *other ions like K^+, Rb^+, Cs^+ are still bigger and also have weak positive field. Hence, they can stabilise bigger superoxide, O_2^- ion and thus form superoxide.*

The **normal oxides** of alkali metals dissolve readily in water to form hydroxides and a large amount of heat is produced.

$$M_2O(s) + H_2O(l) \longrightarrow 2M^+(aq) + 2OH^-(aq) + \text{Heat}$$

3. Basic nature of alkali metal hydroxides. The **peroxides** and **superoxides** are also readily hydrolysed by water as presented below :

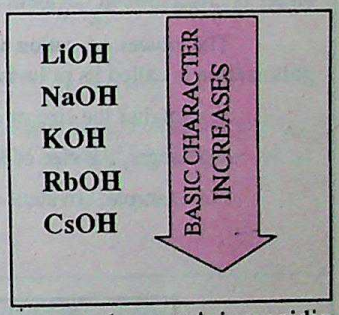
$$Na_2O_2(s) + 2H_2O(l) \longrightarrow 2Na^+(aq) + 2HO^-(aq) + H_2O_2(l)$$

$$2KO_2(s) + 2H_2O(l) \longrightarrow 2K^+(aq) + 2OH^-(aq) + H_2O_2(l) + O_2(g)$$

The higher oxides generally act as good oxidising agents.

The hydroxides of alkali metals are strong bases, all of which are highly soluble in water as well as in alcohol and are stable to heat. Lithium hydroxide, however, is an exception. It is slightly soluble in water and loses a water molecule on heating.

$$2LiOH \xrightarrow{\text{Heat}} Li_2O + H_2O$$



The **basic character of alkali metal hydroxides increases in going down the group.** *This can be explained in terms of decreasing ionisation energies in moving down the group. The decrease in ionisation energies leads to weakening of the bond between alkali metal and hydroxide ion. This results in the increased concentration of hydroxyl ions in solution, i.e., increased basic character.*

4. Reaction with water. Alkali metals react with water and other compounds containing acidic hydrogen atoms such as hydrogen halides (HX) and acetylene (C_2H_2) and liberate hydrogen gas.

$$2Na + 2H_2O \longrightarrow 2NaOH + H_2$$

$$2Na + 2HX \longrightarrow 2NaX + H_2 \; ; \qquad \textit{where } X = \textit{halogen}$$

$$2Na + 2HC \equiv CH \longrightarrow \underset{\text{Sodium acetylide}}{2NaC \equiv CH} + H_2$$

On descending the group from lithium to caesium, the vigour of the reaction increases and in the case of heavier alkali metals, the liberated hydrogen catches fire.

All the alkali metals on exposure to atmosphere react with oxygen and moisture to form oxides and hydroxides and therefore their surface gets tarnished. In order to protect from atmospheric oxygen and water, these metals are stored under kerosene oil.

5. Reaction with halogens. Alkali metals combine with halogens to form metal halides, which are ionic crystalline solids having general formula M^+X^-.

$$2M + X_2 \longrightarrow 2M^+X^-$$

Reactivity of alkali metals with particular halogen increases from Li to Cs. On the other hand reactivity of halogens with particular alkali metal M decreases from F_2 to I_2.

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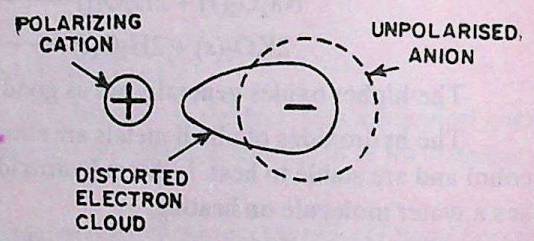
Reactivity with particular halogen X_2	*Reactivity with particular alkali metal M*
Li, Na, K, Rb, Cs ↓ INCREASES	F_2, Cl_2, Br_2, I_2 ↓ DECREASES

All the halides of alkali metals *except lithium fluoride* are freely soluble is water. The low solubility of lithium fluoride is attributed to greater force of attraction between lithium ions and fluoride ions in the crystal lattice.

IONIC/COVALENT CHARACTER IN A BOND ; FAJAN'S RULES

When a cation approaches an anion, it tends to attract the electron cloud of the anion. As a result the electron cloud of anion gets ***distorted*** or ***polarised***. Polarisation of anion brings the electron density to lie between the two nuclei forming the bond. It also causes partial neutralisation of charges on the ions and introduces covalent character in the ionic bond. Now larger the polarisation, larger is the degree of covalent character in ionic bond.



The power of cation to polarise the anion is called its **polaring power** and ability of anion to undergo polarisation is called its **polarisability**. According Fajan's rules, polarisation depends on following factors :

(*i*) Smaller the size of cation, larger is its polaring power.

(*ii*) Larger, the size of anion, larger is its polarisability.

For example, covalent character **increases** among the halides of Li as

LiF < LiCl < LiBr < LiI

Size of anion increases. Thus, covalent character INCREASES

Similarly, among iodides, covalent character increases as

CsI < RbI < KI < NaI < LiI

Size of cation decreases. Thus, covalent character INCREASES

6. Reaction with non-metals. Alkali metals, on heating react with non-metals such as sulphur and phosphorus to form sulphides and phosphides respectively.

$$16M + S_8 \longrightarrow 8M_2S$$

$$12M + P_4 \longrightarrow 4M_3P$$

7. Solubility in Liquid Ammonia. All alkali metals dissolve in liquid ammonia giving *deep blue* solutions which are conducting in nature. These solutions contain ammoniated cations and ammoniated electrons as shown below.

$$M + (x + y)NH_3 \longrightarrow M^+(NH_3)_x + e^{-1}(NH_3)_y$$

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The blue colour of the solution is considered to be due to ammoniated electrons which absorb energy corresponding to red region of visible light for their excitation to higher energy levels. The transmitted light thus, imparts blue colour to the solution. ***The electrical conductivity of the solution*** *is due to both ammoniated cations and ammoniated electrons.* The blue solution on standing slowly liberates hydrogen :

$$2M + 2NH_3 \longrightarrow \underset{\text{(Metal amide)}}{2MNH_2} + H_2$$

8. Complex Compounds. The group 1 metal ions form fewer complex compounds than any other group of metal ions. The complex forming ability decreases in the order.

$$Li > Na > K > Rb > Cs.$$

DIAGONAL RELATIONSHIP

Some of the elements of second period exhibit similarity in properties with diagonally opposite elements of third period. This *similarity in the properties of diagonally opposite elements* is called **diagonal relationship.** The pairs of diagonal elements in the periodic table are shown below.

Period	*Group 1*	*Group 2*	*Group 13*	*Group 14*
2	**Li**	**Be**	**B**	**C**
3	**Na**	**Mg**	**Al**	**Si**

Cause of Diagonal Relationship

The diagonal relationship arise due to resemblance in properties such as *atomic size, ionisation energy, electronegativity* and *polarizing power of their corresponding cations.* For example, Li^+ and Mg^{2+} ions have almost similar ionic size and polarising powers as indicated below.

$$r_{Li^+} = 76 \text{ pm}; \qquad r_{Mg^{2+}} = 72 \text{ pm}.$$

Anomalous Behaviour of Lithium and its Diagonal Relationship with Magnesium

The properties of lithium are quite different from the properties of other alkali metals. On the other hand, it shows greater resemblance with magnesium, which is diagonally opposite element of group 2. The main reasons for the anomalous behaviour of lithium as compared to other alkali metals are :

(*i*) *The extremely small size of lithium atom and its ion.*

(*ii*) *Greater polarizing power of lithium ion (Li^+), due to its small size which result in the covalent character in the compounds.*

(*iii*) *Least electropositive character and highest ionisation energy as compared to other alkali metals.*

The reason for resemblance of properties of lithium with magnesium is, that these two elements have almost same polarizing power.

The following points illustrate the anomalous properties of lithium and its diagonal relationship with magnesium :

1. The m. pt. and b. pt. of lithium are comparatively high.
2. Lithium is much harder than the other alkali metals. Magnesium is also a hard metal.
3. Lithium reacts with oxygen least readily to form normal oxide whereas other alkali metals form peroxides and super-oxides.

Magnesium also forms normal oxide.

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4. LiOH like $Mg(OH)_2$ is a weak base. Hydroxides of other alkali metals are strong bases.
5. Due to their appreciable covalent nature, the halides and alkyls of lithium and magnesium are soluble in organic solvents.
6. Unlike elements of group 1 but like magnesium, lithium forms nitride with nitrogen.

$$6Li + N_2 \longrightarrow 2Li_3N$$

7. Unlike other alkali metals lithium reacts directly with carbon to form an ionic carbide. Magnesium also forms a similar carbide.
8. The carbonates, hydroxides and nitrates of lithium as well as magnesium decompose on heating.

$$Li_2CO_3 \longrightarrow Li_2O + CO_2$$
$$MgCO_3 \longrightarrow MgO + CO_2$$
$$2LiOH \longrightarrow Li_2O + H_2O$$
$$Mg(OH)_2 \longrightarrow MgO + H_2O$$
$$4LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$$
$$2Mg(NO_3)_2 \longrightarrow 2MgO + 4NO_2 + O_2$$

The corresponding salts of other alkali metals are stable towards heat.

9. Li_2CO_3, LiOH, LiF and Li_3PO_4 are the only alkali metal salts which are insoluble in water. The corresponding magnesium compounds are also insoluble in water.
10. Lithium chloride, like magnesium chloride, separates out from aqueous solutions as hydrated crystals, $LiCl.2H_2O$. Sodium and other alkali metal chlorides do not form hydrates at ordinary temperature. LiCl and $MgCl_2$ are deliquescent.

REVIEW QUESTIONS

10.1. Among alkali metal which element has the highest melting point ?
10.2. Explain why alkali metals have low densities.
10.3. What is the common oxidation state exhibited by alkali metals ?
10.4. Explain why group 1 elements have quite high second ionisation energies.
10.5. Which element is the strongest reducing agent ?
10.6. What type of interparticle forces exist in hydrides of group 1 elements ?
10.7. Give equation for the reaction between sodium hydride and water.
10.8. Explain why alkali metals are stored under kerosene.
10.9. Among hydroxides of alkali metals which is the weakest base and which is the strongest base ?
10.10. What happens when
(*i*) Li_2CO_3 is heated (*ii*) Na_2CO_3 is heated ?

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10.2. GROUP 2 ELEMENTS—The Alkaline-Earth Metals

The elements of group 2 are *beryllium* (Be), *magnesium* (Mg), *calcium* (Ca), *strontium* (Sr), *barium* (Ba) and *radium* (Ra). All these elements are metallic in nature. The oxides of these metals were known much earlier than the metals themselves and were named **alkaline earths** because they were alkaline in nature and

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existed in the earth. Later, when the elements were discovered they came to be known as **alkaline earth metals.** These elements have two electrons in the *s*-orbital of the valence shell. Their general electronic configuration may be represented as

$$[\text{Noble gas}]\ ns^2\ ;\ \text{where } n = 2 \text{ to } 7$$

Electronic configurations of these elements are given in Table 10.3.

Table 10.3. Electronic Configurations of Alkaline-Earth Metals

Element	*Symbol*	*Atomic number*	*Electronic Configuration*	*Abundance in earth's crust in (ppm)*
Beryllium	Be	4	[He] $2s^2$	6
Magnesium	Mg	12	[Ne] $3s^2$	20.900
Calcium	Ca	20	[Ar] $4s^2$	36,300
Strontium	Sr	38	[Kr] $5s^2$	300
Barium	Ba	56	[Xe] $6s^2$	250
Radium	Ra	88	[Rn] $7s^2$	1.3×10^{-6}

General Trends in Physical Properties

The valence shell electronic configurations of all these elements are similar, therefore, they exhibit similar physical and chemical properties. Like alkali metals, the compounds of these elements are also predominently ionic. The first member beryllium differs from the rest of the members. The last element of the group, radium is a radioactive element and is studied separately alongwith other radioactive elements.

The variation among the different physical characteristics are as discussed below.

1. Density. The alkaline earth metals are denser and harder than the corresponding alkali metals.

Reason. *The atoms of alkaline earth elements have smaller size and stronger intermetallic bonds, as compared to alkali metals. Therefore, they are more closely packed in their crystal lattices which accounts for high density and hardness of these elements.*

In general, the density first decreases upto calcium and then increases upto radium. The cause for decrease in density upto calcium is presumably due to less better packing arrangement of constituents in solid lattice.

2. Melting point and boiling point. The alkaline earth metals because of their smaller size and a more close packed structure have higher melting and boiling points than the alkali metals. A look at Table 10.4 shows that no regular trends are observed in the variation of melting and boiling points.

3. Atomic and ionic radii. The atomic radii as well as ionic radii of the members of the family are smaller than the corresponding mer[illegible]s of alkali metals.

Reason. *The alkaline earth [illegible]als have a higher nuclear charge due to which the electrons are more strongly attracted towards the nucleus causing a decrease in atomic size.*

Within the group, the atomic as well as ionic radii increase with increase in atomic number. This is due to the addition of new shells, the effect of which is more predominent than the increase in nuclear change.

4. Ionisation energy and electropositive character. The alkaline earth metals owing to their large size of atoms have fairly low values of ionisation energies as compared to the *p*-block elements. However, within the group, the ionisation energy decreases as the atomic number increases. It is because of *increase in*

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atomic size due to addition of new shells and increase in the magnitude of screening effect of the electrons in inner shells.

Alkaline earth metals are fairly electropositive in nature, however, due to their greater ionisation energies these are less electropositive than alkali metals. In general, among the family members the electropositive character increases from Be to Ba.

The values of the second ionisation energies are higher than the first (Table 10.4). *It is because greater energy is required to pull out an electron from positively charged ion than from the neutral atom.*

A comparison of ionisation energies of elements of groups 1 and 2 shows that the members of group 2 have higher values. This is ascribable to smaller size and higher nuclear charge of alkaline earth metals due to which the electrons in their outermost shell are tightly held.

It is interesting to note that although first I.E. alkaline earth metals are higher than those of alkali metals, the second I.E. values are much lower than those of alkali metals (*cf.* Tables 10.2 and 10.4).

Reason. *The second electron in the case of alkali metals is to be removed from a cation which has already acquired a noble gas configuration while in alkaline earth metals, the second electron is to be removed from a monovalent cation which is yet to acquire the stable noble gas configuration. Therefore, the second electron can be removed more easily in the case of group 2 elements than in group 1 elements.*

Table 10.4. Physical Properties of Group 2 Elements (Alkaline Earth Metals)

Element	*Atomic mass*	*Atomic radius*[a] *(pm)*	*Ionic radius*[b] *(pm)*	*Ionisation energy (kJ mol*$^{-1}$*)* *I*	*II*	*Electro-negativity*[c]	*Density*[d] *(g cm*$^{-3}$*)*	*Melting point (K)*	*Boiling point (K)*	*E° (volts)*[e]
Beryllium	9.01	112	27	899	1757	1.57	1.85	1560	2770	– 1.70
Magnesium	24.31	160	72	737	1450	1.31	1.74	920	1378	– 2.37
Calcium	40.08	197	100	590	1146	1.00	1.05	1112	1767	– 2.87
Strontium	87.62	215	118	549	1064	0.95	2.03	1041	1654	– 2.89
Barium	137.33	222	135	503	965	0.89	3.62	1000	1413	– 2.90
Radium	226.03	—	148	509	979	0.9	5.5	973	—	– 2.92

a—Metallic radius (co-ordination no. 12 for all elements except Ba for which co-ordination number is 8).

b—values are for co-ordination number 6 except for Be^{2+} for which co-ordination number is 4.

c—Pauling scale ; *d*—293 K ; *e*—For $M^{2+}(aq) + 2e^- \longrightarrow M(s)$ at 298 K.

5. Oxidation states. The alkaline earth metals have two electrons in their valence shell and by losing these electrons, these atoms acquire the stable noble gas configuration. Thus, unlike alkali metals, the alkaline earth metals exhibit **+ 2** oxidation state in their compounds.

$$\underset{\text{[Noble gas] } ns^2}{M} \longrightarrow \underset{\text{[Noble gas]}}{M^{2+}} + 2e^-$$

Although the second ionisation energies of these elements are high as compared to the first, yet they exist as divalent ions in most of their compounds because of the following **reasons** :

(*i*) *Divalent ions have the stable noble gas configuration.*

(*ii*) *The divalent cations result in stronger lattices than monovalent cations and hence a lot of energy called lattice energy is released which easily compensates for the high second ionisation energy.*

This accounts for the existence of divalent ions in **solid state.**

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(*iii*) *The divalent cation due to smaller size gets hydrated in water to a greater extent and thus the hydration energy released compensates for the second ionisation energy. This accounts for the existence of divalent ions in* **aqueous state.**

The following table gives the comparison of energy changes for formation of **MgCl(aq) and $MgCl_2$(aq).**

MgCl(aq)	*ΔH* (*kJ mol*$^{-1}$)	*$MgCl_2$(aq)*	*ΔH* (*kJ mol*$^{-1}$)
$Mg(s) \longrightarrow Mg(g)$	150	$Mg(s) \longrightarrow Mg(g)$	150
$Mg(g) \longrightarrow Mg^+(g) + e^-$	737	$Mg(g) \xrightarrow{-2e^-} Mg^{2+}(g)$	2188
$\frac{1}{2}Cl_2 \longrightarrow Cl(g)$	122	$Cl_2(g) \longrightarrow 2Cl(g)$	244
$Cl(g) + e^- \longrightarrow Cl^-(g)$	– 348	$2Cl(g) + 2e^- \longrightarrow 2Cl^-(g)$	– 696
$Mg^+(g) + Cl^-(g) + (aq) \longrightarrow MgCl(aq)$	– 735	$Mg^{2+}(g) + 2Cl^-(g) + (aq) \longrightarrow MgCl_2(aq)$	– 2670
Net Energy Change	*– 74*	*Net Energy Change*	*– 784*

6. Reducing properties. All the members of group 2, owing to their low ionisation energies have a tendency to lose their valence electrons and thus act as strong reducing agents. As the reduction potential values decrease down the group (Table 10.4) it indicates the increase in strength as a reducing agent. However, the members of this group are weaker reducing agents than the alkali metals. *It is because of higher ionisation energy of alkaline earth metals as compared to alkali metals.*

7. Flame colouration. Among the members of this group except Be and Mg all other members give characteristic colouration to the flame.

Reason. *Beryllium and magnesium do not impart any colour to the flame because of their small size and higher ionisation energies. Due to this, the energy of flame is insufficient to cause the excitation of their valence electrons to higher shells. On the the hand, Ca (red colour), Sr (crimson colour), Ba (apple green) and Ra (crimson colour) give characteristic flame colouration due to obvious reasons.* (Refer to flame colouration alkali metals).

Chemical properties

Because of their *low ionization energies* and *high electropositive character*, the alkaline earth metals have a great tendency to lose valence electrons and, therefore, the reactivity of these elements increases in going down the group. As compared to alkali metals, these elements are less reactive because they have relatively higher ionization energies. The important chemical reactions of alkaline earth metals are given below :

1. Hydrides. All the members of the group, except beryllium, combine with hydrogen on heating to form metal hydrides, MH_2.

$$M + H_2 \longrightarrow MH_2$$

BeH_2 can, however, be produced by reduction of $BeCl_2$ with $LiAlH_4$.

$$2BeCl_2 + LiAlH_4 \longrightarrow 2BeH_2 + LiCl + AlCl_3$$

Some of the characteristics of hydrides are :

(*i*) MgH_2 is covalent in nature, while CaH_2, SrH_2 and BaH_2 are ionic in nature. CaH_2 is known as ***hydrolith.***

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(*ii*) These hydrides have high reactivity with water. They dissolve in water producing hydrogen gas

$$MH_2(s) + 2H_2O(l) \longrightarrow M^{2+}(aq) + 2OH^-(aq) + 2H_2(g)$$

$$CaH_2(s) + 2H_2O(l) \longrightarrow Ca^{2+}(aq) + 2OH^-(aq) + 2H_2(g)$$

2. Oxides. All the alkaline earth metals burn in oxygen forming oxides. Beryllium, magnesium and calcium form monoxides while strontium and barium form peroxides.

$$2M + O_2 \longrightarrow \underset{\text{(Monoxide)}}{2MO} \qquad (M = Be, Mg \text{ or } Ca)$$

$$M + O_2 \longrightarrow \underset{\text{(Peroxide)}}{MO_2} \qquad (M = Ba \text{ or } Sr)$$

Their monoxides can also be prepared by decomposition of their respective carbonates.

$$MCO_3 \longrightarrow MO + CO_2 \qquad (M = Be, Mg, Ca, Sr \text{ or } Ba)$$

The reactivity of these metals towards oxygen increases as we move down the group.

Some of the characteristics of oxides are :

(*i*) They are very stable due to large lattice energies.

(*ii*) BeO is amphoteric while oxides of other elements are basic in nature. The amphoteric nature of BeO is supported by its reaction with acids as well as alkalies.

$$BeO + 2HCl \longrightarrow BeCl_2 + H_2O$$

$$BeO + 2NaOH \longrightarrow \underset{\text{Sodium beryllate}}{Na_2BeO_2} + H_2O$$

(*iii*) BeO and MgO are almost insoluble in water due to their large lattice energies but oxides of other elements dissolve in water with evolution of heat to form corresponding hydroxides.

$$MO(s) + H_2O(l) \longrightarrow M^{2+}(aq) + 2OH^-(aq) + heat$$

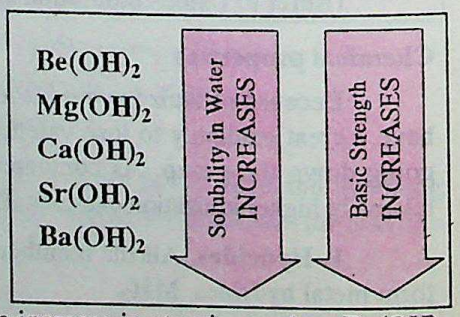
3. Hydroxides. The hydroxides of these elements can be formed either by dissolving metal oxides in water or by reaction of these elements with water. *Some of the characteristics of hydroxides are :*

(*i*) The **hydroxides** of magnesium, calcium, strontium and barium are **bases** and their strength increases from magnesium to barium. *It is because of increase in the ionic radius down the group due to which the strength of M—O bond in MOH decreases and hence causes an increase in basic character.*

(*ii*) These hydroxides are less soluble in water as compared to the alkali metal hydroxides. However, they give strongly alkaline solutions due to their ready ionizability to form $OH^-(aq)$. All these bases neutralize acids to give salts and water.

$$M(OH)_2 + 2HCl \longrightarrow MCl_2 + 2H_2O$$

(M = Mg, Ca, Sr, Ba)



(*iii*) The solubility of the hydroxides in water increases with the increase in atomic number. $Be(OH)_2$ and $Mg(OH)_2$ are almost insoluble, $Ca(OH)_2$, is sparingly soluble while $Sr(OH)_2$ and $Ba(OH)_2$ are increasingly more soluble.

Reason. *Among the hydroxides of this group it is observed that the magnitude of hydration energy remains almost unaltered whereas the magnitude of lattice energy decreases significantly down the group due to increase in size. Thus, the overall net effect of the two factors,* ($\Delta H_{Lattice} - \Delta H_{Hydration} = \Delta H_{Solution}$) $\Delta H_{Solution}$ *becomes more negative from Be to Ba accounting for increase in solubility. In simple words, as the lattice energy decreases the solubility increases and vice versa.*

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Aqueous solutions of calcium hydroxide (*lime water*) and barium hydroxide (*baryta*) are used to detect and estimate carbon dioxide because they give precipitates with CO_2.

$$Ca(OH)_2 + CO_2 \longrightarrow \underset{\text{White ppt.}}{CaCO_3} + H_2O$$

$$Ba(OH)_2 + CO_2 \longrightarrow \underset{\text{White ppt.}}{BaCO_3} + H_2O$$

However, if excess CO_2 is passed, the precipitates dissolve due to the formation of soluble bicarbonates. It is observed that the bicarbonates of alkaline earth metals are stable only in solution and decompose on heating even in the dissolved state. These cannot, therefore, be isolated in the solid form and differ in this respect from the bicarbonates of alkali metals.

$$CaCO_3 + H_2O \underset{\text{Heat}\ -CO_2}{\overset{+CO_2}{\rightleftharpoons}} Ca(HCO_3)_2$$

4. Reaction with Water. All these metals react with water to give the hydroxides and hydrogen. The reactivity increases with increasing atomic number. Beryllium is hardly affected by water at room temperature. It does not react readily even with boiling water. Magnesium on the other hand reacts only with boiling water, whereas calcium, strontium and barium reacts vigorously with water even at room temperature.

$$M(s) + 2H_2O(l) \longrightarrow M^{2+}(aq) + 2OH^-(aq) + H_2(g)$$

However, the reaction of alkaline earth metals with water is less vigorous as compared with that of alkali metals.

5. Carbonates. Carbonates of alkaline earth metals are insoluble in water. These can be precipitated by addition of sodium or ammonium carbonate solution to the solution of salts of these metals. For example,

$$CaCl_2 + Na_2CO_3 \longrightarrow \underset{\text{ppt.}}{CaCO_3} + 2NaCl$$

All the carbonates decompose on heating to give carbon dioxide and metal oxide.

$$MCO_3 \xrightarrow{\Delta} MO + CO_2$$

However, as the atomic number increases, the stability of the carbonates towards heat **increases.** Beryllium carbonate is unstable and can be kept only in an atmosphere of CO_2.

Reason. *The stability of carbonate towards heat depends upon the stability of the resulting metal oxide. More is the stability of the resulting metal oxide lesser is the stability of the carbonate towards heat and vice versa. Now the stability of resulting metal oxides decreases down the group due to decrease in lattice energy,* (because of bigger size) *therefore the stability of carbonates towards heat increases.*

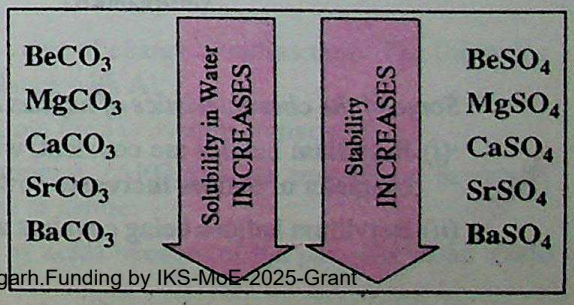
6. Sulphates. Sulphates of alkaline earth metals can be prepared by the reaction of H_2SO_4 with the metals, their oxides, hydroxides or carbonates.

$$Ca + H_2SO_4 \longrightarrow CaSO_4 + H_2$$

$$CaO + H_2SO_4 \longrightarrow CaSO_4 + H_2O$$

$$Ca(OH)_2 + H_2SO_4 \longrightarrow CaSO_4 + 2H_2O$$

$$CaCO_3 + H_2SO_4 \longrightarrow CaSO_4 + CO_2 + H_2O$$



The sulphates of alkaline earth metals are less soluble than the corresponding salts of alkali metals. Their solubilities decrease on going down the group.

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Reason. *It is because in going down the group from Be to Ra, the magnitude of hydration energy decreases significantly, due to increase in the atomic size of alkaline earth metals, bringing about a decrease in solubility of their sulphates.*

Unlike carbonates, sulphates of alkaline earth metals are stable to heat.

7. Halides. Alkaline earth metals react with halogens directly to form halides having general formula, MX_2.

$$M + X_2 \longrightarrow MX_2$$

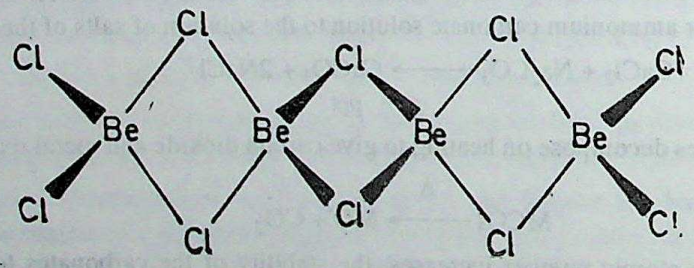
Alkaline earth metal halides can also be obtained by the action of halogen acids on metals, their oxides, carbonates and hydroxides.

$$M + 2HX \longrightarrow MX_2 + H_2$$
$$MO + 2HX \longrightarrow MX_2 + H_2O$$
$$MCO_3 + 2HX \longrightarrow MX_2 + H_2O + CO_2$$
$$M(OH)_2 + 2HX \longrightarrow MX_2 + 2H_2O$$

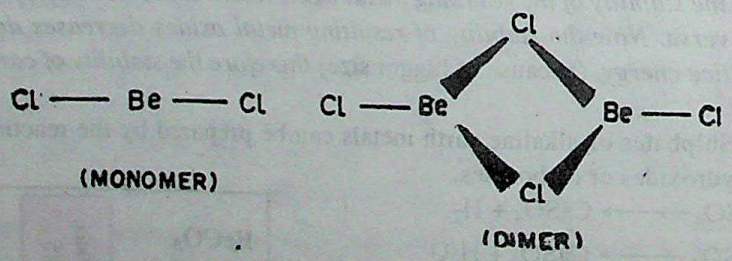
Beryllium chloride is prepared indirectly, from its oxide as follows :

$$BeO + C + Cl_2 \xrightarrow{870—1070\ K} BeCl_2 + CO$$

Structure of $BeCl_2$. Beryllium chloride possesses different structures in solid and vapour state. In *solid state*, it exists in the form of polymeric chain structure in which each Be atom is surrounded by four chlorine atoms. Two of the chlorine atoms are bonded by covalent bonds while the other two by co-ordinate bonds. The bridged structure consisting of infinite chains is shown below :



In the **vapour state,** however it exists as a monomer with a linear structure and zero dipole moment above 1200 K. But below 1200 K, it exists as dimeric structure even in vapour state.



Some of the characteristics of halides are :

(*i*) Beryllium halides are covalent, while halides of other alkaline earth metals are ionic. The ionic character of halides increases down the group due to gradual increase in ionic size.

(*ii*) Beryllium halides being covalent are soluble in organic solvents.

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(*iii*) Fluorides of other elements are generally insoluble in water due to high magnitude of lattice energy but bromides, chlorides and iodides are soluble in water.

(*iv*) The anhydrous halides are **hygroscopic** and form hydrates such as $MgCl_2.6H_2O$ and $CaCl_2.6H_2O$. Because of this property anhydrous calcium chloride is used as dehydrating agent. Beryllium chloride fumes is moist air due to its hydrolysis.

$$BeCl_2 + \underset{\text{(Moisture)}}{2H_2O} \longrightarrow \underset{\text{(Fumes)}}{Be(OH)_2} + 2HCl$$

8. Nitrides. The alkaline earth elements burn in nitrogen to form ionic nitrides with formula M_3N_2.

$$3Ca + N_2 \longrightarrow Ca_3N_2$$

$$3Mg + N_2 \longrightarrow Mg_3N_2$$

The nitrides are, in general, crystalline solids and are decomposed by water to produces ammonia and metal hydroxide

$$Ca_3N_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2NH_3 \uparrow$$

9. Complex Compounds. Group 2 elements have a tendency to form stable complexes. Their ability to form complexes is more as compared to alkali metals. This is because of the smaller size and higher charge of the alkaline earth metal ions as compared to alkali metal ions. Among the elements of group 2, beryllium and magnesium, have greater tendency of complexation.

Anomalous Behaviour of Beryllium

The properties of beryllium, the first member of the alkaline earth metals, differ from the rest of the members. It is mainly because of

1. *its small size* ;
2. *relatively high electronegativity and ionisation energy as compared to other members and*
3. *absence of vacant d-orbitals in its valence shell.*

Some important points of ***differences between beryllium and magnesium*** are given below :

(*i*) Be is higher than Mg.

(*ii*) M.P./B.P. of Be are higher than Mg.

(*iii*) Be does not react with water even at high temperature while Mg decomposes boiling water.

(*iv*) BeO is amphoteric while MgO is weakly basic.

(*v*) Beryllium carbide reacts with water to give methane while magnesium carbide produces acetylene.

$$Be_2C + 2H_2O \longrightarrow 2BeO + \underset{\text{Methane}}{CH_4}$$

$$MgC_2 + H_2O \longrightarrow Mg(OH)_4 + \underset{\text{Acetylene}}{C_2H_2}$$

Resemblance of Be with Al

Be resembles Al to some extent due to nearly the same value of charge to radius ratio. The following points illustrate the anomalous behaviour of Be and its resemblance with Al.

1. Unlike group-2 elements but like aluminium, beryllium forms covalent compounds.
2. The hydroxides of beryllium, ($Be(OH)_2$) and aluminium, ($Al(OH)_3$) are amphoteric in nature, whereas those of other elements of group-2 are basic in nature.
3. Like aluminium, beryllium is not readily attacked by acids because of the presence of an oxide film.

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4. Beryllium and aluminium form fluoro-complex ions, $[BeF_4]^{2-}$ and AlF_6^{3-} in solution, whereas the other elements of group-2 do not form stable fluoro complexes in solution.
5. The oxides of both Be and Al, *i.e.*, BeO and Al_2O_3 are high melting insoluble solids.
6. Carbides of both Al and Be give methane on hydrolysis.
7. $BeCl_2$ like Al_2Cl_6 has a bridged polymeric structure.
8. The salts of beryllium as well as aluminium are extensively hydrolysed.

REVIEW QUESTIONS

10.11. Which element among alkaline-earth metals has least density ?

10.12. Out of Na and Mg which has higher ionisation energy ?

10.13. What is the common oxidation state exhibited by group-2 elements ?

10.14. Which element among group-2 elements has highest first ionisation energy ?

10.15. Give equations to show that amphoteric character of beryllium oxide.

10.16. What happens when water is added to quick lime (CaO) ?

10.17. What is baryta ? Give its one use.

10.18. Which carbonate of alkaline earth element can be kept only in the atmosphere of CO_2 ?

10.19. How is beryllium chloride prepared ?

10.20. How do $Be(OH)_2$ and $Mg(OH)_2$ differ from each other ?

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10.3. GROUP-13 ELEMENTS—The Boron Family

The elements *boron* (B), *aluminium* (Al), *gallium* (Ga), *indium* (In) and *thallium* (Tl) constitute group 13 of the periodic table. Except boron, which is classified as a non-metal all other elements of this group are metals. Non-metallic character of boron is due to its small atomic size and high ionisation energy. All the elements of this group have three electrons in their valence shells. The general valence shell electronic configuration of these elements is ns^2np^1. Thus, these elements belong to '*p*' block of the periodic table. Electronic configurations of elements of this group are given below in Table 10.5.

Table 10.5. Electronic Configurations of Group 13 Elements

Element	*Symbol*	*Atomic Number*	*Electronic Configuration*	*Abundance in Earth's crust (in ppm)*
Boron	B	5	$[He]\ 2s^2\ 2p^1$	10
Aluminium	Al	13	$[Ne]\ 3s^2\ 3p^1$	81,300
Gallium	Ga	31	$[Ar]\ 3d^{10}\ 4s^2\ 4p^1$	15
Indium	I	49	$[Kr]\ 4d^{10}\ 5s^2\ 5p^1$	1
Thallium	Tl	81	$[Xe]\ 4f^{14}\ 5d^{10}\ 6s^2\ 6p^1$	0.3

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General Trends in Physical Properties

The values of different physical constants of group 13 elements are listed in Table 10.6 on next page. The gradation of different physical characteristics are as discussed below :

1. Density. The density of members of this group increases down the group evidently due to increase in mass per unit volume. Aluminium has an exceptionally low density.

2. Melting Points and Boiling Points. The melting points decrease from B to Ga and then increase from Ga to Tl. However, the boiling points show a gradual decrease from B to Tl.

3. Atomic Radii and Ionic Radii. The atomic radii of members belonging to group 13 are smaller than the corresponding group 2 elements.

Reason. *It is because when we move from group 2 elements to group 13 elements in the same period, the magnitude of the nuclear charge increases whereas the addition of electron occurs to the same shell. Since electrons in the same shell do not screen each other, thereby the electrons experience a strong nuclear pull and hence the size decreases. However, on moving from B to Tl the size increases due to progressive addition of new energy shells.*

The observed atomic radius of Ga is slightly smaller than that of Al. *It is because in going from Al to Ga the electrons are also filled into d-subshell. Since these intervening electrons do not screen the nuclear charge effectively, therefore, the electrons in Ga experience more force of attraction than in Al, causing a decrease in its radius.*

The ionic radii follow a regular trend.

4. Ionisation Energy and Electropositive Character. The first ionisation energy of these elements is less than those of corresponding members of the alkaline earth metals *i.e.*, group 2 elements.

Reason. *The values of ionisation energies of group 13 elements are lower than those of group 2 elements. It is because in elements of group 13 the first electron is to be removed from a p-orbital whereas in the case of group 2 elements, it is to be removed from s-orbital. Since the electrons in s-orbital are more tightly held by the nucleus due to greater penetration of s-orbital, therefore, more energy is required to remove an electron from s-orbital than from a p-orbital.* However, the second and third ionisation energies of these elements are quite high because the second and third electrons are removed from *ns*-orbital.

Among the members of this group, the ionisation energies decrease down the group due to increase in size. However, it has been observed that the ionisation energy of Ga is higher than that of Al. This is because of smaller size of Ga as compared to Al higher nuclear charge.

These elements are less electropositive (metallic) than elements of groups 1 and 2 due to their relatively smaller size and higher ionisation energies. As we move down the group, the electropositive character increases due to decrease in ionisation energy. Boron, the first member of the group is a non-metal whereas other elements are metals.

5. Oxidation Sates. The atoms of group 13 elements have three valence electrons *i.e.*, two in *s*-subshell and one in *p*-subshell. Thus, from the configuration it appears that + 3 should be the most common oxidation state of these elements. However, due to small size of boron it cannot lose its valence electrons to from B^{3+} ion, rather it combines with other atoms through covalent bonds. Many compounds of aluminium like $AlCl_3$ are also covalent in anhydrous state.

Except boron, the other elements also exhibit **+1** oxidation state. As we move from B to Tl, the **+1** oxidation state becomes more stable.

Reason. *+1 oxidation state is exhibited when the s-electrons of the valence shall do not participate in bond formation. Such a reluctance on the part of electron pair to participate in bond formation is called* **inert pair effect**. *The inert pair effect becomes more predominant down the group because the nuclear*

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Table 10.6. Some Properties of Group 13 Elements (Boron Family)

Element	*Atomic mass*	*Atomic radius*[a] *(pm)*	*Ionic radius*[b] *(pm)* M^{3+}	M^{+}	*Ionisation energy* ($kJ\ mol^{-1}$) *I*	*II*	*III*	*IV*	*Electro-negativity*°	*Density* ($g\ cm^{-3}$)	*Melting point (K)*	*Boiling point (K)*	$E°$ *(volts)*[d]	$E°$ *(volts)*[e]
Boron	10.81	85	27	—	800	2427	3659	25026	2.0	2.35	2453	3923	—	—
Aluminium	26.98	143	53.5	—	577	1816	2744	11578	1.5	2.70	933	2740	– 1.66	– 0.55
Gallium	69.72	135	62.0	120	578	1979	2962	6200	1.6	5.90	303	2676	– 0.56	—
Indium	114.82	167	80.0	140	558	1820	2704	5200	1.7	7.31	430	2353	– 0.34	– 0.18
Thallium	204.38	170	88.5	150	590	1971	2877	—	1.8	11.85	576	1730	+ 1.26	– 0.34

(*a*) Metallic radius, (*b*) 6-coordination, (*c*) Pauling scale,

(*d*) For $M^{3+}(aq) + 3e^{-} \longrightarrow M(s)$ at 298 K; (*e*) For $M^{+}(aq) + e^{-} \longrightarrow M(s)$ at 298 K.

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charge increases much more than the corresponding increase in distance of outer electrons from the nucleus. Thus, the effect of increase in nuclear charge is not neutralised by the increase in distance due to which the s-electrons of the valence shell become more penetrating i.e., are held more tightly and hence, show reluctance for participation in bonding.

6. Reducing Properties. The order of decreasing reducing power of group 13 elements is as follows :

$$\mathbf{Al > Ga > In > Tl}$$

Since we know that the measurement of reduction potential involves three different energy changes during the process *i.e.* $\Delta H_{sublimation}$, I.E. and $\Delta H_{hydration}$ therefore, the net resultant of these three factors gives us the resultant value of reduction potential. Now more negative is the value of reduction potential, greater is the reducing character (see Table 10.6).

Chemical Properties

Among the members constituting this group, boron predominantly forms covalent bonds in its compounds. This is mainly due to its *smaller size and high ionisation energy*. Besides this, a large number of electron deficient compounds of boron are also known.

Unlike boron, the other members of the group are metallic and the electropositive character increases as we go down the group. All these elements in their compounds exhibit the oxidation state of + 3 and + 1. The important chemical properties of the boron family are discussed below.

1. Hydrides. None of the group 13 elements reacts directly with hydrogen. However, a number of hydrides of these elements have been prepared by indirect methods. The boron hydrides are sometimes called *boranes*.

The boranes can be classified with two series :

(*a*) $B_n H_{n+4}$, called ***nidoboranes*** (*b*) $B_n H_{n+6}$, called ***arachnoboranes***

The simplest borane is **diborane,** B_2H_6 *(BH_3 being unstable has not been isolated)*. It is prepared on the industrial scale by the reaction of lithium hydride with BF_3 :

$$2BF_3(g) + 6LiH(s) \xrightarrow{450\ K} B_2H_6(g) + 6LiF(s)$$

In laboratory, it can be obtained by following methods.

(*i*) *By the reaction of iodine with sodium borohydride in a high boiling solvent.*

$$2NaBH_4 + I_2 \longrightarrow B_2H_6 + 2NaI + H_2$$

(*ii*) *By reduction of BCl_3 with $LiAlH_4$*

$$4BCl_3 + 3LiAlH_4 \longrightarrow 2B_2H_6 + 3AlCl_3 + 3LiCl$$

(*iii*) *By passing silent electrical discharge through BCl_3 and H_2*

$$2BCl_3 + 6H_2 \xrightarrow[\text{Electric discharge}]{\text{Silent}} B_2H_6 + 6HCl$$

Mixture of higher boranes can be prepared by action of phosphoric acid on magnesium boride

$$Mg_3B_2 + H_3PO_4 \longrightarrow \underset{(\text{Mainly } B_4H_{10})}{\text{Mixture of boranes}} \xrightarrow{\text{Heat}} \underset{\text{Diborane}}{B_2H_6}$$

Structure of B_2H_6

The structures of boranes are of great interest since there are not enough valence electron to form the expected number of covalent bonds. The structure of diborane as determined by electron diffraction studies is shown in Fig. 10.1.

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According to this structure, 16 electrons are required for the formation of conventional covalent bonds whereas in diborane there are only 12 valence electrons, three from each boron and six from the six hydrogen atoms. In this way, it is an *electron deficient* compound.

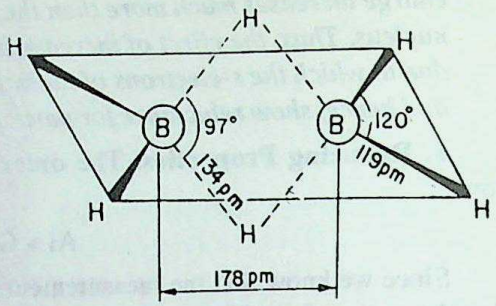
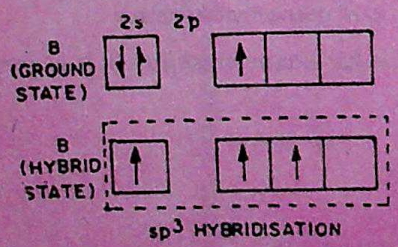


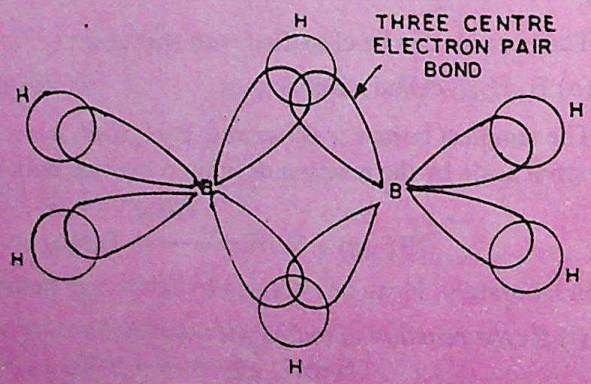
Fig. 10.1. Structure of diborane.

The two bridging hydrogen atoms (shown by dotted lines) lie symmetrically above and below the plane whereas the other four hydrogen atoms are present in a plane perpendicular to rest of the molecule. Each bridged hydrogen is bonded to the two boron atoms only be sharing of two electrons. Such a covalent bond is called **three centre electron pair bond** or **a multi-centre bond.** Due to close proximity of the bridged H atoms the positive charges on the two hydrogen nuclei suffer strong electrostatic repulsions. To minimize these repulsions, the orbitals of bridges are bent away from each other in the middle.

Structure of B_2H_6 on the basis of Hybridisation

On the basis of hybridisation, the structure of B_2H_6 can be explained as follows. Boron atom (excited configuration : $2s^1\ 2p_x^1\ 2p_y^1\ 2p_z^0$) assumes sp^3 hybrid state in B_2H_6. One of the four sp^3 hybrid orbitals is vacant and has been shown by broken lines. Two of the sp^3 hybrid orbitals from sigma bonds with 1*s*-orbitals H-atoms. The third hybrid orbital containing unpaired electron overlaps simultaneously with 1*s*-orbital of H-atom and vacant hybrid orbital of the adjacent boron atom to constitute ***three centre electron pair bond.*** Which is represented as B.....H.....B. The H-atom involved in it is *bridge hydrogen.*





Some important characteristics of boranes are given below :

(*i*) Lower boranes are colourless gases while higher boranes are volatile liquids or solids.

(*ii*) They undergo spontaneous combustion in air due to strong affinity of boron for oxygen.

$$B_2H_6 + 3O_2 \longrightarrow B_2O_3 + 3H_2O + heat$$

(*iii*) Boranes are readily hydrolysed by water liberating H_2 gas

$$B_2H_6 + 6H_2O \longrightarrow \underset{\text{Boric acid}}{2H_3BO_3} + 6H_2$$

(*iv*) Boranes react with alkali metal hydrides in diethylether to form borohydride complexes.

$$B_2H_6 + 2MH \longrightarrow \underset{\text{Metal borohydride}}{2M^+[BH_4]^-} \qquad (M = Li \text{ or } Na)$$

Alkali borohydrides are used as reducing agents.

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(*v*) Diborane reacts with ammonia under different condition to give different products

$$B_2H_6 \xrightarrow[\text{Low temp.}]{\text{Excess of } NH_3} \underset{\text{(Addition compound)}}{B_2H_6 \cdot 2NH_3}$$

$$B_2H_6 \xrightarrow[\text{High temp.}]{\text{Excess of } NH_3} \underset{\text{Borontride}}{(BN)_x}$$

$$B_2H_6 + 6NH_3 \xrightarrow{450\ K} \underset{\text{Borazine}}{3B_3N_3H_6} + 12H_2$$

Borazine has cyclic structure* similar to benzene and thus, it is called **inorganic benzene.**

In contrast to hydrides of boron, the *other elements* of this group form only a few stable hydrides. AlH_3 is formed by Al. It is a colourless polymeric solid of the formula $(AlH_3)_x$ and contains Al—H—Al bridges. In addition, a complex hydride of aluminium, $Li[AlH_4]$ is known. It is prepared by reaction of $AlCl_3$ with excess of LiH in ether. It is a *very powerful reducing agent.*

$$4LiH + AlCl_3 \xrightarrow{\text{Ether}} Li[AlH_4] + 3LiCl$$

Gallium is also known to form a complex hydride, $Li[GaH_4]$.

2. Oxides and hydroxides. Almost all the elements of group 13 form oxides and hydroxides of the composition M_2O_3 and $M(OH)_3$ respectively. The nature of these oxides/hydroxides changes from weakly acidic to amphoteric and amphoteric to basic in moving down the group from B to Tl.

$B(OH)_3$ and B_2O_3	>	$Al(OH)_3$ and Al_2O_3	>	$Ga(OH)_3$ and Ga_2O_3	>	$In(OH)_3$ and In_2O_3	>	$Tl(OH)_3$ and Tl_2O_3
Acidic		*Amphoteric*		*Amphoteric*		*Basic*		*Strong base*

BASIC CHARACTER INCREASES

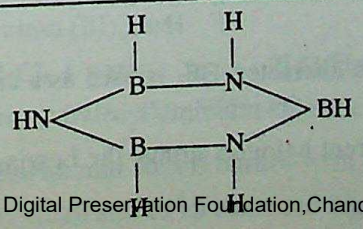
Reason. *As we move down the group, the atomic size of elements goes on increasing whereas the ionisation energy decreases. As a result, the strength of M—O bond goes on decreasing accounting for the increase in basic character down the group or conversely explains the decrease in acidic character.*

The **preparation** of oxides of B and Al are being described as follows.

(*i*) The oxide of boron, B_2O_3 is obtained by burning of boron in the presence of oxygen.

$$4B + 3O_2 \longrightarrow 2B_2O_3$$

*Borazine is



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It is a good dehydrating agent and reacts with water to form orthoboric acid (H_3BO_3). B_2O_3 being predominantly an acidic oxide dissolves in alkalies to give borates as well as metaborates.

$$B_2O_3 + 6NaOH \longrightarrow \underset{\text{Sodium borate}}{2Na_3BO_3} + 3H_2O$$

$$B_2O_3 + 2NaOH \longrightarrow \underset{\text{Sodium metaborate}}{2NaBO_2} + H_2O$$

(*ii*) Aluminium oxide, Al_2O_3 is also obtained by heating aluminium in the presence of oxygen.

$$4Al + 3O_2 \longrightarrow 2Al_2O_3$$

It is soluble in acids as well as bases and hence, is amphoteric in nature.

$$Al_2O_3 + 3H_2SO_4 \longrightarrow Al_2(SO_4)_3 + 3H_2O$$

$$Al_2O_3 + 2NaOH \xrightarrow{\text{Fuse}} \underset{\text{Sodium meta aluminate}}{2NaAlO_2} + H_2O$$

Crystalline alumina, Al_2O_3, exists in many forms, one of these called **corrundum** is very hard and is used as an abrasive. It can be prepared by heating amorphous alumina to about 2000 K.

3. Halides. Both boron and aluminum combine with halogens to form trihalides having the general formula MX_3. These halides can be prepared by heating the elements directly with halogens.

$$2B + 3X_2 \longrightarrow 2BX_3 ; \quad \text{(where X = Cl, Br)}$$

$$2Al + 3X_2 \longrightarrow 2AlX_3 ; \quad \text{(where X = Cl, Br, I)}$$

(*i*) **Boron trihalides.** The halides of boron are covalent in nature. This has been indicated by the fact that they are soluble in organic solvents and that they are bad conductor of electricity.

The boron trihalides are covalent in nature and exist as monomeric molecules having planar triangular geometry. In these halides boron assumes sp^2 hybrid state and the three B—X bonds are formed by axial overlap of sp^2 hybrid orbital of boron and *p*-orbital of halogen as shown in Fig. 10.2. Since there are only six electrons in the valence shell of boron atom in boron trihalides, therefore, they have a great tendency to accept two more electrons in order to acquire stable octet. Hence boron trihalides act as Lewis acids. They rapidly combine with electron donors such as NH_3, F^- ion, amines, ether, sulphides or phosphorus.

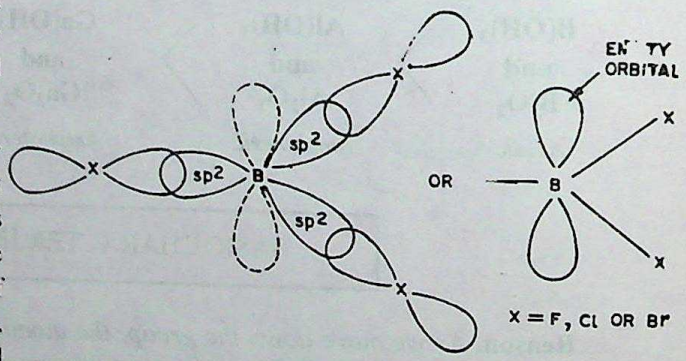

Fig. 10.2. Structure of boron trihalides.

$$\begin{array}{c} F \\ \ddot{F} \end{array} : \ddot{B} + : \ddot{N} : H \begin{array}{c} H \\ \ddot{H} \end{array} \longrightarrow \begin{array}{c} F \\ \ddot{F} \end{array} : \ddot{B} : \ddot{N} : H \begin{array}{c} H \\ \ddot{H} \end{array}$$

As a consequence of its strong Lewis acid character, BF_3 is used as a catalyst in several industrial processes.

Among the trihalides of boron with different halogen atoms, the Lewis acid character follows the order :

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$$BF_3 < BCl_3 < BBr_3$$

ACID STRENGTH INCREASES

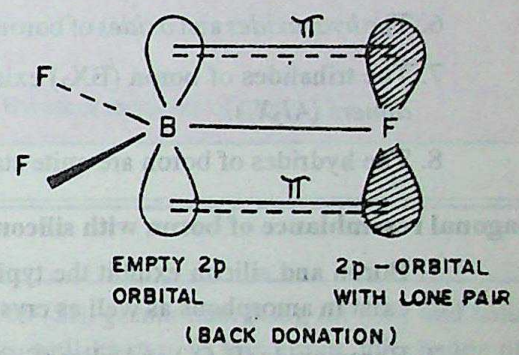
This order is just the **reverse** of what is expected on the basis of electronegativities of the halogens.

BF_3 should be most acidic because F being most electronegative should create maximum electron deficiency on B atom. But actually, BF_3 is found to be the least acidic among the trihalides of boron.

This is explained on the basis of halogen-boron **back-π-bonding.** *One of the 2p orbital of F atom having lone pair overlaps sidewise with the empty 2p-orbital of boron atom to form* **pπ-pπ back bonding.** This is also known as **back donation.**

As a result of this back donation, the electron deficiency of boron gets compensated and its Lewis acid character decreases.

Since the tendency for back donation is maximum in the case of fluorine due to its small size and more inter-electronic repulsions, therefore, it is the least acidic. The tendency of back bonding falls as we move from BF_3 to BCl_3 and BCl_3 to BBr_3 due to increase in the size of halogen atoms consequently, the acidic character increases accordingly.



(*ii*) **Aluminium halides.** These halides exist as dimers. For example, aluminium chloride exists as Al_2Cl_6. In the dimeric structure each aluminium atom accepts a lone pair of electrons from the chlorine atom bonded to the other aluminium atom as shown in Fig. 10.3. In doing so each aluminium atom completes its octet.

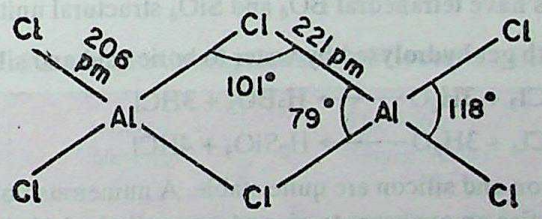


Fig. 10.3. Dimeric structure of aluminium chloride.

Note. *Boron halides do not form dimers because the size of boron is so small that it is unable to co-ordinate four large- sized halide ions.*

The dimer structure exists in vapour state below 473 K. At higher temperature Al_2Cl_6 dissociates to trigonal planar $AlCl_3$ molecule.

In polar solvents such as water, the dimer dissociates due to high heat of hydration resulting in the formation of hexaquo aluminium (III) ions.

$$Al_2Cl_6 + \text{water} \rightleftharpoons 2[Al(H_2O)_6]^{3+}(aq) + 6Cl^-(aq)$$

It is due to this reason hydrated aluminium chloride is ionic in nature.

Anomalous Behaviour of Boron and Resemblance with Silicon

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Because of extremely small size of its atom and high electronegativity, boron differs in its properties from other elements of the group. On the other hand, it resembles silicon to some extent due to diagonal

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relationship. The following properties illustrate the anomalous behaviour of boron and its diagonal relationship with silicon.

Anomalous properties of boron

1. Boron is a *non-metal* whereas aluminium is a *metal*.
2. *Boron is a bad conductor of electricity* whereas aluminium is a good conductor.
3. Boron exists in two forms—crystalline and amorphous. Aluminium is a soft metal and does not exist in different forms.
4. The *melting point* and *boiling point* of boron are much *higher* than those of aluminium.
5. Boron forms only *covalent* compounds whereas aluminium forms even some ionic compounds.
6. The *hydroxides* and *oxides* of boron are *acidic* in nature whereas those of aluminium are amphoteric.
7. The trihalides of boron (BX_3) exist as *monomers*. On the other hand, aluminium halides exist as *dimers* (Al_2X_6).
8. The hydrides of boron are quite stable while those of aluminium are unstable.

Diagonal resemblance of boron with silicon

1. Boron and silicon exhibit the typical properties of non-metals. These do not form cations. Both exist in amorphous as well as crystalline forms.
2. Boron oxide (B_2O_3) and silica (SiO_2), both are acidic and dissolve in alkali solutions to form borates and silicates respectively.

$$B_2O_3 + 6NaOH \longrightarrow 2Na_3BO_3 + 3H_2O$$
$$SiO_2 + 2NaOH \longrightarrow Na_2SiO_3 + H_2O$$

Borates and silicates have tetrahedral BO_4 and SiO_4 structural units respectively.

3. The chlorides of both get hydrolysed by water to boric acid and silicic acid respectively.

$$BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$$
$$SiCl_4 + 3H_2O \longrightarrow H_2SiO_3 + 4HCl$$

4. The hydrides of boron and silicon are quite stable. A numerous volatile hydrides of these are also known which catch fire on exposure to air and are easily hydrolysed.
5. Boron forms binary compounds with several metals known as borides just as silicon forms metal silicides.

$$3Mg + 2B \longrightarrow \underset{\text{Magnesium boride}}{Mg_3B_2}$$
$$2Mg + Si \longrightarrow \underset{\text{Magnesium silicide}}{Mg_2Si}$$

Some of these borides and silicides are known to react with H_3PO_4 or H_2SO_4 to yield boranes and silanes.

$$Mg_3B_2 + H_3PO_4 \longrightarrow \text{Mixture of borones (Mainly } B_4H_{10})$$
$$Mg_2Si + H_3PO_4 \longrightarrow \text{Mixture of silanes}$$

6. Both elemental boron and silicon are semi-conductors.

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REVIEW QUESTIONS

10.21. How does electropositive character change with increase in atomic number among the group 13 elements ?

10.22. Which element among group 13 elements has the highest value of I.E. ?

10.23. Which element of group 13 forms acidic oxide ?

10.24. Give chemical equations illustrating the amphoteric character of Al_2O_3.

10.25. What is the formula of boric acid ?

10.26. How is diborane prepared ?

10.27. Among the trihalides of boron given below, which is the strongest Lewis acid ?

BF_3, BCl_3, BBr_3.

10.28. Draw the structure of Al_2Cl_6.

10.29. Give a physical characteristics of boron in which it differs from the other members of group 13.

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10.4. GROUP 14 ELEMENTS—The Carbon Family

The elements belonging to group 14 are *carbon* (C), *silicon* (Si), *germanium* (Ge), *tin* (Sn) and *lead* (Pb). Except germanium, all other elements of this group are quite well-known. In this group, the change of character from non-metallic to metallic is well evident from the fact that the first two elements, carbon and silicon are non-metals, germanium is a semi-metal whereas tin and lead are metals.

All the elements of the group have four electrons in their valence shells. Their general valance shell electronic configuration is $ns^2\ np^2$. The electronic configuration of the elements of the group are given below in Table 10.7.

Table 10.7. Electronic Configurations of Group 14 Elements

Element	*Symbol*	*Atomic Number*	*Electronic Configuration*	*Abundance in Earth's crust (in ppm)*
Carbon	C	6	[He] $2s^2\ 2p^2$	320
Silicon	Si	14	[Ne] $3s^2\ 3p^2$	277, 200
Germanium	Ge	32	[Ar] $3d^{10}\ 4s^2\ 4p^2$	7
Tin	Sn	50	[Kr] $4d^{10}\ 5s^2\ 5p^2$	40
Lead	Pb	82	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^2$	16

Carbon and silicon are quite abundant in earth's crust whereas germanium occurs only as traces. Tin and lead also occur only in small amounts. Carbon is the only element of this group which occurs in free state as *coal, diamond* and *graphite*. It also occurs in combined state as carbonates, CO_2 and hydrocarbons. Silicon is the second most abundant element in earth's crust and occurs mainly as *silica* and *silicates*. Germanium occurs only as traces in certain ores and coal, however, it is important for making conductors and transistors. Tin is mined as *cassiterite* or *tin stone* (SnO_2). Lead occurs as *galena* (PbS).

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General Trends in Physical Properties

The values of some important physical constants of the carbon family are recorded in Table 10.8. The variation of the physical properties among the members of the group is discussed below :

1. Density. The density of the members belonging to this group is found to increase down the group as usual. It is because of the increase in mass per unit volume.

2. Melting Points and Boiling Points. The melting and boiling points of group 14 elements are much higher as compared to those of group 13 elements. *It is because the atoms of group 14 can form four covalent bonds with each other and, therefore, there are strong binding forces between their atoms in both solids as well as liquid states.* Consequently, their melting and boiling points are more. However, the melting and boiling points decreases down the group.

3. Atomic Radii. The atomic radii of group 14 elements are smaller than the corresponding elements of group 13. This is because as we move from group 13 to group 14 elements within the same period, the nuclear charge increases and consequently the size decreases.

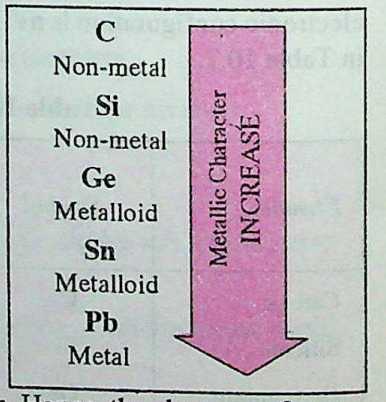
Within the group, the atomic radii increases on going down the group due to increase in the number of energy shells.

4. Ionisation Energy. As the sizes of elements belonging to group 14 are smaller than the corresponding elements of group 13, their first ionisation energies are higher than those of corresponding members of group 13. Among the members of the same group, the ionisation energies (I.E.) follow the order

$$C > Si > Ge > Sn < Pb^*$$

In general, the ionisation energy decreases down the group due to increase in size and screening effect of inner electrons. The electropositive character (or metallic) increases down the group due to decrease in ionisation energy.

5. Metallic Character. The elements of group 14 are less metallic due to relatively large values of ionisation energies as compared to elements of group 13. The metallic character however increase down the group from C to Pb.



6. Oxidation States. The electronic configuration of the valence shell reveals the presence of four valence electrons. Now, in order to acquire the noble gas configuration the carbon family members have to gain or lose four electrons forming ions of the type M^{4+} or M^{4-}. Since the formation of such ions would require a large amount of energy which shall not be available under the conditions of bond formation, therefore they neither lose nor gain four electrons but share electrons to get stable noble gas configuration. Hence, the elements of group 14 form covalent bonds in their compounds, with the highest oxidation state of + 4.

The elements of this group also exhibit an oxidation state of + 2. It is observed that the lower oxidation state becomes more stable with increase in atomic number, down the group. This is due to the *inert pair effect.*

The elements in their lower oxidation state of + 2 are expected to form ionic bonds whereas in the higher oxidation state of + 4 these can form only covalent bonds in their compounds. This indirectly means that as we move down the group, the tendency to form ionic compounds increases.

*The higher value of IE_1 of Pb is due to extremely poor shielding of inner *f*-orbitals as a result of which effective nuclear charge experienced by outer shell electrons of Pb increases.

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Table 10.8. Some Properties of Group 13 Elements (Boron Family)

Element	*Atomic mass*	*Covalent radius*[a]	*Ionic radius*[b] *(pm)*		*Ionisation energy* ($kJ\ mol^{-1}$)				*Electro-negativity*[c]	*Density* ($g\ cm^{-3}$)[d]	*Melting point (K)*	*Boiling point (K)*	*Electrical resistivity*
			M^{4+}	M^{2+}	*I*	*II*	*III*	*IV*					
Carbon	12.01	77	—	—	1086	2352	4620	6220	2.5	3.51[e]	4373	—	10^{14}—20^{16}
Silicon	28.09	118	40	—	786	1577	3228	4354	1.8	2.34	1693	3550	50
Germanium	72.60	122	53	73	761	1537	3300	4409	1.8	5.32	1218	3123	50
Tin	118.71	140	69	118	708	1411	2942	3929	1.8	7.26[f]	505	2896	10^{-5}
Lead	207.02	146	78	119	715	1450	3081	4082	1.9	11.34	600	2024	2×10^{-5}

(a) For M^{IV} oxidation state, (b) 6-coordination, (c) Pauling scale, (d) 298 K, (e) For diamond ; for graphite density is 2.22, (f) β-form (stable at room temperature).

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7. Catenation. A remarkable property of carbon is its ability to form compounds in which carbon atoms are linked to one another in chains or rings. *This property of forming the chains of identical atoms is called* **catenation.** The property of catenation depends upon the strength of atom-atom bond. The greater the strength of the atom-atom bond, greater is the extent of catenation. The elements of group 14 exhibit catenation. It is most extensive in the case of carbon because C—C bond is very strong. On going down the group, the atom-atom bond strength decreases and hence the extent of catenation also decreases. It varies in the order

$$\mathbf{C >> Si > Ge \simeq Sn >> Pb}$$

Bond	*C—C*	*Si—Si*	*Ge—Ge*	*Sn—Sn*
Bond Energy ($kJ\ mol^{-1}$)	353.3	225.7	167.2	155

8. Allotropy. A characteristic property of the elements of groups 14 is that these show allotropy*. For example, carbon exists as diamond and graphite. Similarly, the other members of the family also show allotropic forms.

Chemical Properties

As already discussed the formation of M^{4-} or M^{4+} ions is not favoured energetically. These elements, therefore, form mostly covalent compounds with a covalency of four. These elements acquire tetravalency by promotion of one of the *s*-electrons to *p*-orbital in the valence shell. These four half-filled orbitals then undergo sp^3 hybridization resulting in the formation of four equivalent orbitals which are directed towards the four corners of a regular tetrahedron. Therefore, *molecules like* CH_4, CCl_4, $SiCl_4$, $SnCl_4$ *and* $PbCl_4$ *have tetrahedral shapes.*

Carbon the first member differs distinctly from other group 14 elements on account of its ability to form $p\pi$-$p\pi$ multiple bonds to itself and to other elements like nitrogen and oxygen. A number of compounds containing C = C, C ≡ C, C = O, C = N, C ≡ N and C = S functional groups are known. Although such kinds of bonds are largely unknown for other members yet a few compounds containing double bond between silicon, germanium or tin atoms have been isolated in recent years.

Unlike carbon, the other elements of group 14 do not form stable $p\pi$-$p\pi$ multiple bond due to their relatively large atomic size. These elements, however, can use the *d*-orbitals and form $d\pi$-$p\pi$ multiple bond. A few compounds of silicon linked to oxygen and nitrogen are known where a sufficient evidence of multiple bonding by utilisation of *d*-orbitals, is available. For example, *trisilyl amine,* $N(SiH_3)_3$ is planar whereas *trimethyl amines* $N(CH_3)_3$ is pyramidal. This can be explained as follows.

In **trimethyl amine,** N atom assumes sp^3 hydrid state. Three of the hybrid orbitals are used in forming σ bonds with CH_3 groups, while the lone pair is present in the fourth hybrid orbital. Thus, the molecule is pyramidal. The basic character is due to availability of lone pair on N atom. In **trisilyl amine,** the N atom assumes sp^2 hybrid state and the lone pair of N is involved in $d\pi$-$p\pi$ bonding by getting itself delocalised on to empty 3*d*-orbitals of silicon. The overlap of empty *d*-orbital of silicon with completely filled 2*p*-orbital of sp^2 hybridised N atom is shown on page 771.

*Allotropy is the existence of an element in two or more forms, which are significantly different in physical properties but have similar chemical properties. The difference may be due to difference in crystal structure, the number of atoms in the molecule of a gas or the molecular structure of a liquid.

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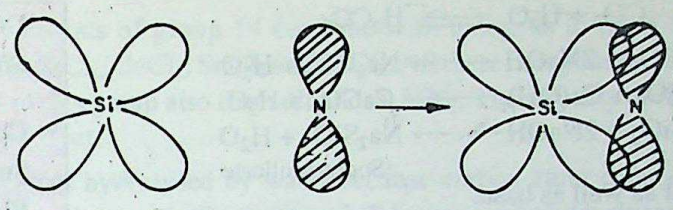
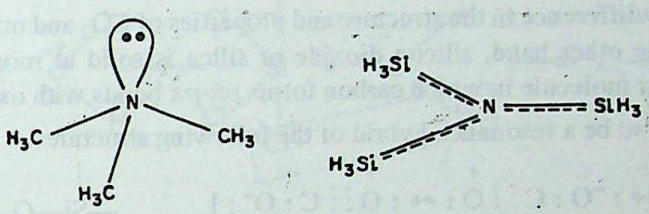


EMPTY d-ORBITAL OF Si — FILLED ORBITAL OF N — dπ–pπ BOND

Since the electron pair of N atom in $(SiH_3)_3$ is involved in multiple bonding, therefore, its availability is considerably reduced thereby decreasing the basic character. The molecule is planar due to sp^2 hybrid state of N atom. The structures of $(CH_3)_3N$ and $(SiH_3)_3N$ are shown below.



PYRAMIDAL — PLANAR

The **chemical characteristics** of the group 14 elements are discussed below.

1. Hydrides. The elements of group 14 combine with hydrogen to form covalent hydrides. Carbon forms a large number of cyclic and acyclic hydrides known as hydrocarbons. These have general formulas of the type C_nH_{2n+2} (alkanes), C_nH_{2n} (alkenes), C_nH_{2n-2} (alkynes), etc. Silicon and germanium form fewer hydrides of the general formula M_nH_{2n+2} (where M = Si, n = 1 to 8 or M to Ge, n = 1 to 5).

These are known as silanes and germanes respectively. Only one hydride of tin, namely monostannane (SnH_4) is known. There is, however, some doubt about the existence of PbH_4 (Plumbane). These hydrides decompose on heating. Thermal stability of hydrides of this group decreases on moving down the group as is evident from the fact that hydrides of carbon (hydrocarbons) are very stable whereas hydrides of tin and lead are very unstable. The reducing character of these hydrides increases on going down the group.

2. Oxides. The elements of group 14 form two types of oxides, *monoxides* and *dioxides* which differ from each other both structurally as well as in their properties.

(*i*) *Monoxides.* All the elements of this group except Si form monoxides of the general formula **MO**, such as CO, SiO, GeO, SnO and PbO. Except CO which is neutral, other monoxides are basic. Carbon monoxide has the highest bond energy (1070 kJ mol^{-1}) among the diatomic molecules. The molecular orbital configuration of CO molecule is : $\sigma_{1s}^2\, \sigma_{1s}^{2*}\, \sigma_{2s}\, \sigma_{2s}^{2*}\, \pi_{2p_x}^2\, \pi_{2p_y}^2\, \pi_{2p_z}^2$, which suggest the presence of triple bond between carbon and oxygen atoms. However, CO molecule is considered to be a resonance hybrid of the following structures :

$$[:C::\ddot{O}: \longleftrightarrow :\overset{-}{C}\vdots\vdots\overset{+}{O}: \longleftrightarrow :\overset{+}{C}:\ddot{\underset{\cdot\cdot}{O}}^{-}\vdots]$$

Carbon monoxide is a colourless toxic gas and is known to form a number of co-ordination compounds with transition metals *e.g.*, $Ni(CO)_4$, $Fe(CO)_5$ and $Cr(CO)_6$. Such compounds are called as **organometallic** compounds because carbon is bonded to metals.

(*ii*) *Dioxides.* All the elements of this group form dioxides, of the general formula $\mathbf{MO_2}$, such as CO_2, SiO_2, GeO_2, SnO_2 and PbO_2. Some characteristic features of dioxides are :

(*a*) Among these oxides, CO_2 and SiO_2 are acidic whereas GeO_2, SnO_2 and PbO_2 are amphoteric in nature. This is indicated by their reactions given below :

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$$CO_2 + H_2O \rightleftharpoons H_2CO_3$$
$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$
$$CO_2 + Ca(OH)_2 \longrightarrow CaCO_3 + H_2O$$
$$SiO_2 + 2NaOH \longrightarrow \underset{\text{Sodium silicate}}{Na_2SiO_3} + H_2O$$

CO_2, SiO_2	*Acids*
GeO_2, SnO_2, PbO_2	*Amphoteric*

SnO_2 reacts with acid as well as base.

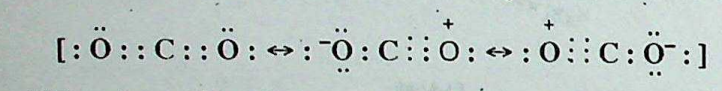
$$SnO_2 + 4HCl \longrightarrow SnCl_4 + 2H_2O$$
$$SnO_2 + 2NaOH \longrightarrow Na_2SnO_3 + H_2O$$

(*b*) PbO_2 is a powerful oxidising agent. It readily dissolves in acids forming Pb(II) salts with the libration of oxygen.

$$PbO_2 + 2HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + \frac{1}{2}O_2$$

(*c*) There is a marked difference in the structure and properties of CO_2 and other dioxides. CO_2 is a gas at room temperature. On the other hand, silicon dioxide or silica is solid at room temperature. CO_2 is a monomeric, linear, non-polar molecule in which carbon forms $p\pi$-$p\pi$ bonds with oxygen.

It may be considered to be a resonance hybrid of the following structures.



Silicon is unable to form $p\pi$-$p\pi$ bond with oxygen atom due to its relatively large size. Thus, it satisfies its tetra covalency with four oxygen atoms and constitutes three dimensional net work structure in which each silicon atom forms four Si—O bonds (Fig. 10.4) which are tertrahedrally disposed. In turn each oxygen atom of SiO_2 is shared by two silicon atoms.

Since Si—O bonds are very strong (368 kJ mol^{-1}), therefore, silica is relatively inert and has a very high m.pt. The dioxides of Ge, Sn and Pb, *i.e.*, GeO_2, SnO_2 and PbO_2 are all network solids with octahedral co-ordination.

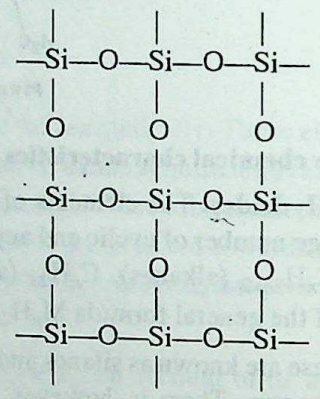


Fig. 10.4. Crystal structure of silica.

Comparison of Properties CO_2 and SiO_2

CO_2	SiO_2
1. It exists as gas.	1. It is a solid.
2. It is a linear, monomeric non-polar molecule.	2. It is a three dimensional net work solid.
3. Appreciably soluble in water.	3. In soluble in water.
4. On reduction with coke gives carbon monoxide $CO_2 + C \longrightarrow 2CO$	4. On reduction with coke in electrical furnace gives silicon carbide $SiO_2 + 3C \longrightarrow SiC + 2CO$

(*iii*) **Carbon Suboxide (C_3O_2).** In addition to CO and CO_2 carbon also forms carbon suboxide which is made by dehydration of malonic acid with P_4O_{10}.

$$\underset{\text{Malonic acid}}{HOOC—CH_2—COOH} \xrightarrow[P_4O_{10}]{150°\,C} \underset{\text{Carbon suboxide}}{O = C = C = C = O} + 2H_2O$$

It is foul smelling gas with b.p. 6°C. It is linear molecule. It gives back malonic acid on reaction with H_2O or HCl.

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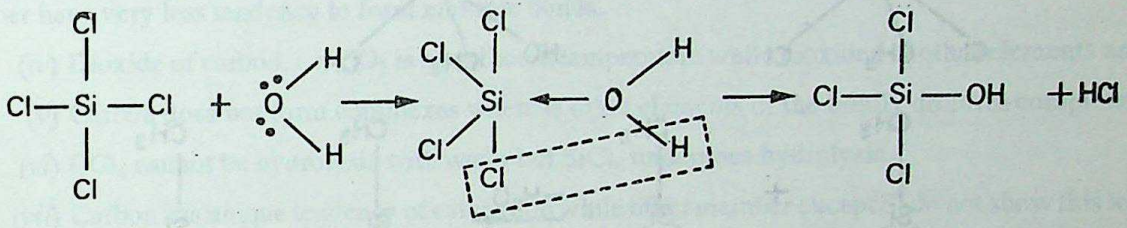
3. Halides. The elements of group 14 combine with halogens to form tetrahalides, of the general formula MX_4, such as CCl_4, $SiCl_4$, $GeCl_4$, $SnCl_4$ and $PbCl_4$. All these compounds are covalent in nature. Except carbon all other elements of this group also form dihalides, MX_2. The stability of the dihalides increases down the group due to inert pair effect.

Carbon halides are not hydrolysed by water because carbon atom cannot increase its co-ordination number beyond four. On the other hand, all other tetrahalides are easily hydrolysed because of the availability of vacant *d*-orbitals in the valence shell of their central atom due to which these can easily extend their co-ordination number beyond four. In order to understand this, let us consider the hydrolysis of $SiCl_4$.

In the first step, H_2O molecule attacks on the central atoms and forms a co-ordinate bond as shown below :



In the second step, a molecule of HCl is eliminated resulting in the replacement of one chlorine atom with OH group. This process continues till all the Cl atoms are replaced by OH groups to form $Si(OH)_4$, *i.e.*, $H_2SiO_3.H_2O$ (Hydrated silicic acid).

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

Due to the same reason tetrahalides of all the elements of group 14 except carbon can react with halogen acids. For example,

$$SiF_4 + 2HF \longrightarrow \underset{\text{Hydrofluoro silicic acid}}{H_2SiF_6}$$

Co-ordination number of silicon in H_2SiF_6 is six. It may be noted that *dihalides have greater ionic character and hence have higher m. pts. and b. pts.* For example, *$SnCl_2$ is a solid whereas $SnCl_4$ is liquid at room temperature.*

4. Silicates and Silicones

(*i*) **Silicates**

Silicate is the general term given to solids with silicon-oxygen bonds. A large percentage of the earth's crust consists of silicate minerals. Some of the important silicate minerals are quartz, asbestos (calcium magnesium silicate, $CaMgSi_2O_6$), feldspar (potassium aluminium silicate, $KAlSi_3O_8$) and zeolites (sodium aluminium silicate, $Na_2Al_2Si_2O_8.xH_2O$).

The silicates are complex network solids having silicate ion $(SiO_4)^{4-}$ as the basic structural unit. The silicate ion has a tetrahedral structure. As a result of sharing of one or more oxygen atoms between such tetrahedrons, a complex structure arises. The basic classification of silicates into *chain silicates, ring silicates, cyclic silicates, sheet silicates, three dimensional silicates* depends on the way in which the $(SiO_4)^{4-}$ tetrahedral units are linked together.

(*ii*) **Silicones**

Silicones are polymeric compounds containing repeated R_2SiO units. The name silicone has been coined for these polymeric compounds because their empirical formula is analogous to that of ketones (R_2CO).

The starting material for the manufacture of silicones is alkyl substituted chlorosilanes. These alkyl chlorosilanes are obtained by the reaction of alkyl halides with silicon in the presence of metallic copper which acts as a catalyst.

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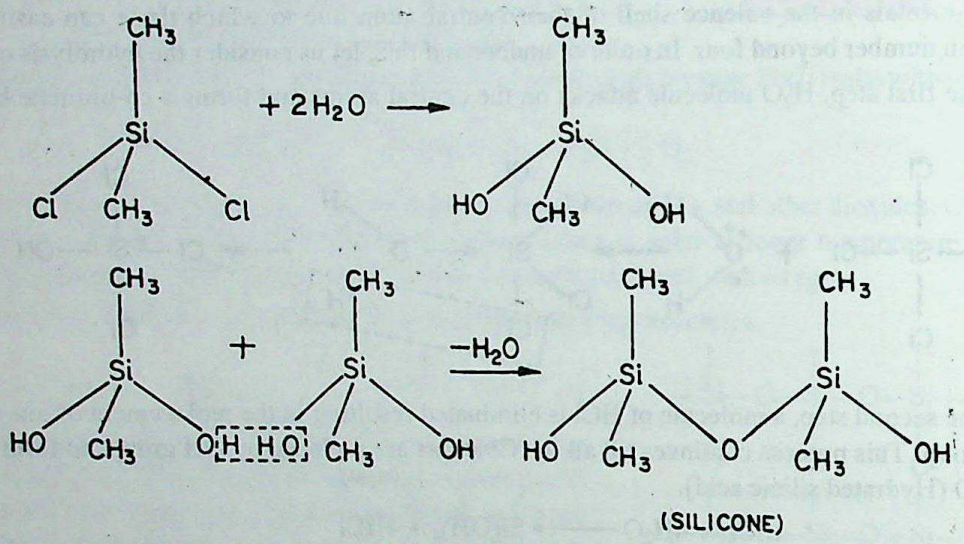
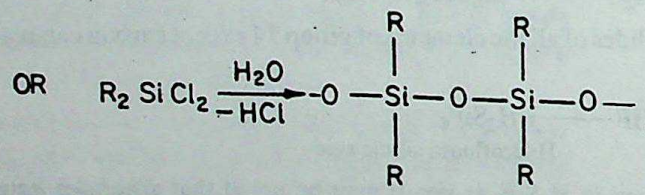
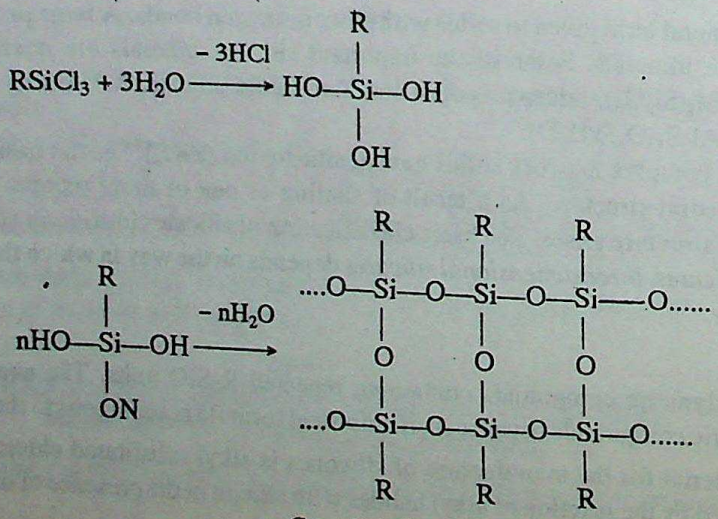
$$2RCl + Si \xrightarrow[570\ K]{Cu\ Powder} R_2SiCl_2$$

On carrying out the hydrolysis of these alkyl dichlorosilanes the Si—Cl bonds are ruptured and the chlorine atoms are replaced by OH groups. As soon as Si—OH bonds are formed, condensation sets in with the elimination of water, yielding silicone, as shown below :





The condensation can be stopped any stage by regulating the conditions to get the polymeric chains of desired length. It is interesting to note that hydrolysis of *alkyl trichlorosilanes,* $RSiCl_3$ gives cross linked polymers instead of chain polymer.



Cross linked polymer

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The silicones are chemically inert, water repellant, heat resistant and good electrical insulators. Thus, owing to these characteristic properties these are used as *lubricants, insulators,* and also as *protective coatings,* etc.

Anomalous Behaviour of Carbon

Carbon, the first member of group 14 elements differs from the other elements in following respects :

(*i*) It is quite hard. Diamond is the hardest substance while other members are soft.

(*ii*) M. Pt. and B. Pt. of C are much higher than those of rest of the members.

(*iii*) Carbon from multiple bonds with other elements such as S, N, O and also with carbon but other member have very less tendency to form multiple bonds.

(*iv*) Dioxide of carbon, *i.e.* CO_2 is gas at room temperature while dioxides of other elements are solids.

(*v*) Carbon does not form complexes whereas other elements of the family do form complexes.

(*vi*) CCl_4 cannot be hydrolysis with water but $SiCl_4$ undergoes hydrolysis.

(*vii*) Carbon has unique tendency of catenation while other member except Si do not show this tendency.

The anomalous behaviour of carbon is attributed to

(*a*) *its small size*

(*b*) *the non-availability of vacant d-orbitals*

(*c*) *high ionisation energy and*

(*d*) *high electronegativity.*

REVIEW QUESTIONS

10.30. Which element in the periodic table has the highest melting point ?

10.31. What are the oxidation states exhibited by group 14 elements ?

10.32. Out of group 14 element which element shows catenation to maximum extent ?

10.33. Name the two crystalline allotropic forms of carbon.

10.34. Among group 14 elements which element has highest tendency to form $p\pi$-$p\pi$ bonds ?

10.35. Out of methane (CH_4) and silane (SiH_4) which is more stable has smaller boiling point ?

10.36. Give three uses of silicones.

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10.5. GROUP 15 ELEMENTS—The Nitrogen Family

The elements *nitrogen* (N), *phosphorus* (P), *arsenic* (As), *antimony* (Sb) and *bismuth* (Bi) constitute group 15 of the periodic table. The first two elements of this group, nitrogen and phosphorus are non-metals, the next two, arsenic and antimony are metalloids whereas the last element, bismuth, is a metal. All the elements of this group have five electrons in their valence shells. Their general valence shell electronic configuration is ns^2np^3. The electronic configurations of group 15 elements are given in Table 10.9.

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Table 10.9. Electronic Configurations of Group 15 Elements

Element	*Symbol*	*Atomic Number*	*Electronic Configuration*	*Abundance (ppm)*
Nitrogen	N	7	[He] $2s^2\,2p^3$	300
Phosphorus	P	15	[Ne] $3s^2\,3p^3$	1200
Arsenic	As	33	[Ar] $3d^{10}\,4s^2\,4p^3$	5
Antimony	Sb	51	[Kr] $4d^{10}\,5s^2\,5p^3$	1
Bismuth	Bi	83	[Xe] $4f^{14}\,5d^{10}\,6s^2\,6p^3$	0.2

General Trends in Physical Properties

1. Density. The density of the members increases down the group, as usual.

2. Melting points and boiling points. These increase on going down the group. However, the melting point of bismuth is usually low. *This may presumably be due to more tendency of Bi to form three rather than five covalent bonds (inert pair effect). Thus, there are weak forces of attraction between their atoms in solid state, accounting for its low m. pt.*

The variation in b. pt. shows a regular trend.

3. Atomic radii. Atomic radii, as expected, increases with increase in atomic number.

4. Ionisation energy and electropositive character. The first ionisation energy decreases regularly down the group due to increase in the size of atoms and screening effect of intervening electrons. The values of ionisation energies of group 15 elements along with other properties are given in Table 10.10.

It must be noted that the ionisation energies of this group are much higher than those of corresponding elements of group 14.

Reason. *This is due to the increase in nuclear charge and extra stable configurations of the elements of this group. The extra stability of configurations is attributed to the exactly half-filled p-orbitals in their valence shells.*

Due to **high ionisation energies,** the elements of this group are less electropositive than elements of group 14. Electropositive (or metallic) character increases on going down the group due to decrease in ionisation energies. The fact is reflected by the change in metallic character from nitrogen to bismuth as shown below.

N — P ; **As — Sb** ; **Bi**

Non-metals **Metalloids** **Metal**

5. Oxidation States. All the elements of this group have five electrons in their valence shell. These elements require three more electrons to acquire noble gas configuration. However, though gaining of three electrons requires a large amount of energy yet it takes place only with nitrogen as it is the smallest and the most electronegative element of this group. N^{3-} ion exists in the compounds such as Mg_3N_2, Ca_3N_2, etc. The other elements of the group form covalent compounds in which their formal oxidation state is – 3. For example, calcium phosphide (Ca_3P_2), sodium arsenide (Na_3As), zinc antimonide (Zn_3Sb_2) and magnesium bismuthide (Mg_3Bi_2).

In addition to – 3 oxidation state, the elements of this group also exhibit + 3 and + 5 oxidation states. However, they cannot form M^{5+} ions due to the large amount of energy required to do so. The tendency to form M^{3+} ions increases on moving down the group due to *inert pair effect*. Sb and Bi exist as M^{3+} ions in

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Table 10.10. Some Properties of Group 15 Elements (Nitrogen Family)

Element	*Atomic mass*	*Ionization energy KJ (mol^{-1})*			*Electro-negativity*	*Covalent radius[a] (ppm)*	*Ionic radius (pm)*	*Melting point (K)*	*Boiling point (K)*	*Density (298 K) ($g\ cm^{-3}$)*
		I	*II*	*III*						
Nitrogen	14.01	1402	2856	4577	3.0	70	171 (N^{3-})	63	77.2	0.879[e]
Phosphorus	30.97	1012	1903	2910	2.1	110	212 (P^{3-})	317.1[b]	553.5[b]	1.823
Arsenic	74.92	947	1798	2736	2.0	120	222 (As^{-3})	1089[c]	888[d]	5.778[f]
Antimony	121.75	834	1595	2443	1.9	140	76 (Sb^{+3})	903.7	1860	6.697
Bismuth	208.98	703	1610	2446	1.9	150	103 (Bi^{3+})	544.4	1837	9.808

(*a*) M^{III} single bond, (*b*) White phosphorus, (*c*) Grey α-form at 38.6 atm, (*d*) sublimation temperature, (*e*) 63 K, (*f*) gray α-form.

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SbF_3 and BiF_3. Most of the other compounds with + 3 and + 5 oxidation states of these elements are covalent. For example, oxidation state of P in PCl_5 is + 5 and in PCl_3 is + 3. Both these compounds are covalent.

In the case of nitrogen all the oxidation states from – 3 to + 5 are possible.

Compound	NH_3	N_2H_4	NH_2OH	N_2	N_2O	NO	HNO_2	NO_2	HNO_3
Oxidation State of N	– 3	– 2	– 1	0	+ 1	+ 2	+ 3	+ 4	+ 5

6. Catenation. The elements of group 15 also exhibit catenation but to a less extent than carbon group. Nitrogen forms chains extending upto three atoms, the common example being hydrazoic acid, N_3H ($H—N = \overset{+}{N} = \underset{..}{\overset{-}{N}}$:) Phosphorus shows a distinct tendency for catenation forming both cyclic and open chain compounds containing several phosphorus atoms.

Reason. *The lesser tendencies of group 15 elements to catenate as compared with carbon can be understood in terms of their bond energies, as listed below :*

Bond	*C—C*	*N—N*	*P—P*	*As—As*
Energy ($kJ\ mol^{-1}$)	*355.3*	*163.8*	*201.6*	*147.4*

As there is a big drop in the bond energy from carbon to nitrogen, evidently the tendency of catenation decreases enormously.

7. Allotropy. Except nitrogen and bismuth, all other elements of the group show allotropy as described below.

Phosphorus exists as : White, red and black phosphorus

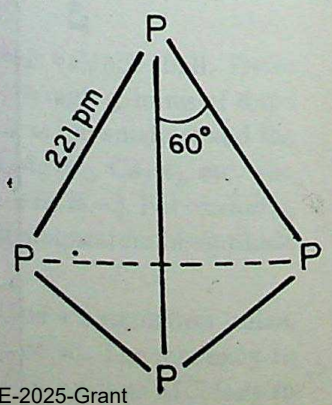
Arsenic exists as : Yellow and grey

Antimony exists as : Yellow and grey.

Chemical Properties

The various elements of this group differ from one another in their chemical reactivity. Nitrogen is chemically **less reactive.** *It is because of high stability of its molecule, N_2 in which the two nitrogen atoms are linked by triple bond* (N ≡ N) and *thus, possess high bond strength (941.4 $kJ\ mol^{-1}$).*

Among the elements of this group only nitrogen has a tendency to form $p\pi$-$p\pi$ multiple bonds with itself as well as with carbon and oxygen. The multiple bonding in nitrogen occurs due to its small size. Nitrogen, thus, forms a diatomic molecule, N_2. On the other hand, phosphorus, arsenic and antimony form tetrahedral molecules in their elemental state with formula M_4. The structure of P_4 is shown in diagram. Each P atom is linked to three other atoms with P—P—P bond angle equal to 60°. Though phosphorus and heavier members of the family do not form $p\pi$-$p\pi$ multiple bonds easily, yet the multiple bonding of the type $d\pi$—$p\pi$ can readily occur in these elements. This type of bonding is prominent for phosphorus as is reflected in the formation of compounds such as POX_3 and $RN = PX_2$.



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Recently, a few compounds of phosphorus and arsenic having multiple bonding like P = C, P ≡ C, P = N, P = P and As = As groups have been synthesized.

The common chemical characteristics of group 15 elements are discussed below :

1. Hydrides. The elements of group 15 form hydrides having the general formula MH_3. All these are covalent in nature. These hydrides are :

NH_3	PH_3	AsH_3	SbH_3	BiH_3
Ammonia	Phosphine	Arsine	Stibine	Bismuthine

Formation of Hydrides. These hydrides can be obtained by the reactions given below

$$Ca_3N_2 + 6H_2O \longrightarrow Ca(OH)_2 + 2NH_3$$

$$Ca_3P_2 + 6H_2O \longrightarrow 2PH_3 + 3Ca(OH)_2$$

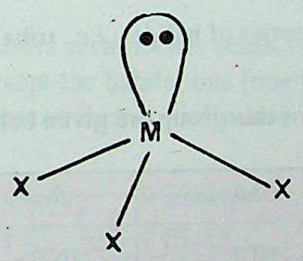
$$P_4 + 3KOH + 3H_2O \longrightarrow \underset{\text{Pot. hypophosphite}}{PH_3 + 3KH_2PO_2}$$

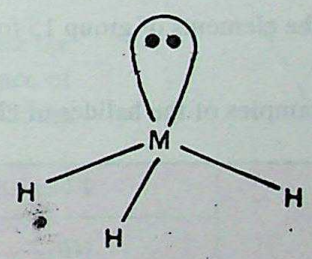
$$Zn_3M_2(s) + 6HCl(aq) \longrightarrow 2MH_3(g) + 3ZnCl_2(aq) \qquad (M = As, Sb \text{ or } Bi)$$

Besides these, N_2H_4 another hydride of nitrogen can be prepared by the action of NH_3 and sodium hypochlorite.

$$NH_3 + NaOCl \longrightarrow \underset{\text{Hydrazine}}{N_2H_4} + NaCl + H_2O$$

Structure of hydrides. In all these hydrides the central atom assumes sp^3 hybrid state forming four sp^3 hybrid orbitals. Three of these hybrid orbitals form sigma bonds with hydrogen atom whereas the fourth hybrid orbital contains lone pair. Thus, these hydrides have pyramidal structure, as shown below.





The angle around the central atom H—M—H decreases from NH_3 to SbH_3 as,

Hydride	**NH_3**	**PH_3**	**AsH_3**	**SbH_3**
H—M—H angle	107°	92°	91°	90°

Reason. *The variation in bond angle can be explained on the basis of electronegativity of the central atom. Nitrogen atom is highly electronegative. Therefore, in NH_3, there is a high electron density around the N atom. This causes greater repulsions between the electron pairs around N atom resulting in the maximum bond angle. As electronegativity decreases down the group, the electron density around the central atom also decreases and consequently, the repulsive interactions between the electron pairs also decrease there by decreasing the bond angle H—M—H.*

The variation of some characteristics of the hydrides are summed up as follows :

(*i*) The **thermal stability** of the hydrides decreases in the order :

$$NH_3 > PH_3 > AsH_3 > SbH_3 > BiH_3$$

It is because the strength of M—H bond decreases down the group due to increase in the size of central atom.

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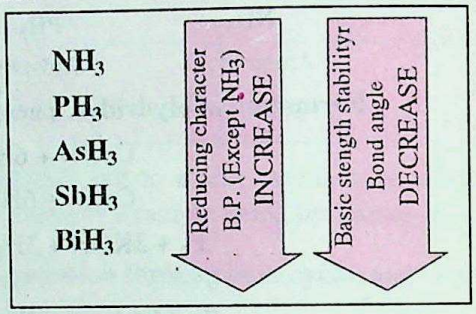
(*ii*) These hydrides act as **reducing agents.** The least stable hydride (BiH_3) acts as the strongest reducing agent whereas the most stable hydride (NH_3) acts as a weakest reducing agent.

(*iii*) The **boiling points** of these hydrides vary as follows :

Hydride	NH_3	PH_3	AsH_3	SbH_3	BiH_3
Boiling point (K)	238.5	185.5	210	254	290

Reason. *NH_3 molecules are associated by intermolecular H-bonds. As a result its boiling point is exceptionally high. The interparticle forces in PH_3 are van der Waal forces due to which its boiling point is low. In moving from PH_3 to BiH_3 boiling points increase. This is due to the increase in the magnitude of van der Waal forces due to increase in molecular size.*



(*iv*) Due to the presence of a lone pair of electrons on the central atom in these hydrides, these act as good **Lewis bases.** The basic character decreases down the group. For example, NH_3 is distinctly basic, PH_3 is a weak base whereas AsH_3, SbH_3 and BiH_3 are very weak bases.

Reason. *Nitrogen because of its small size has the lone pair of electrons concentrated on a small region so density per unit volume is more. Now as we move down the group the size of the central atom keeps on increasing and, therefore, the same electronic charge now is distributed or diffused over larger volume. As a result, the electron density decreases. Thus, the electron donor capacity or the basic strength decreases down the group.*

2. Halides. All the elements of group 15 form two series of halides, *i.e.*, trihalides and pentahalides of the type MX_3 and MX_5.

The common examples of the halides of elements of this group are given below :

	Flourine	*Chlorine*	*Bromine*	*Iodine*
MX_3 series	NF_3 PF_3 AsF_3 SbF_3 BiF_3	NCl_3 PCl_3 $AsCl_3$ $SbCl_3$ $BiCl_3$	NBr_3 PBr_3 $AsBr_3$ $SbBr_3$ $BiBr_3$	— PI_3 AsI_3 SbI_3 BiI_3
MX_5 series	PF_5 AsF_5 SbF_5 BiF_5	PCl_5 $AsCl_5$ $SbCl_5$ —	PBr_5 — — —	— — — —

(*a*) **Trihalides.** Some of the *characteristic of trihalides* are given below :

(*i*) These trihalides are mainly covalent with the exception of BiF_3 which is ionic.

(*ii*) The ionic character of trihalides increases in going down the group.

(*iii*) Like hydrides, these trihalides have *pyramidal* structure.

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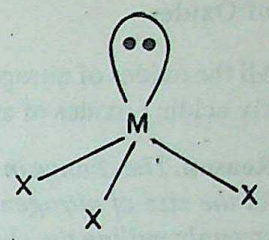
(*iv*) These trihalides except NX_3 can be easily hydrolysed by water according to the reactions given below :

$$PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$$
$$AsCl_3 + H_2O \longrightarrow As_2O_3 + 6HCl$$
$$SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$$
$$BiCl_3 + H_2O \longrightarrow BiOCl + 2HCl$$



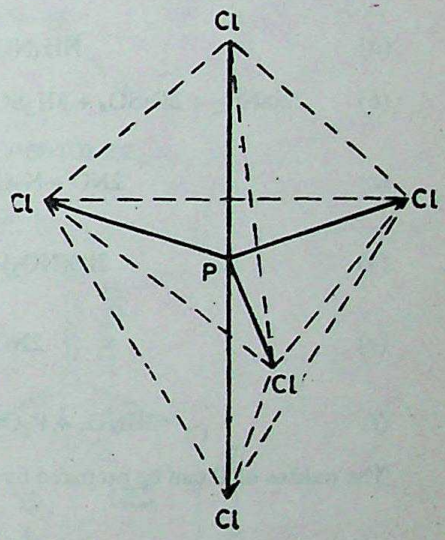
PYRAMIDAL STRUCTURE OF TRIHALIDES

The inability of trihalides of N to hydrolyse is attributed to the non-availability of vacant d-orbitals in nitrogen.

(*v*) The trihalides of P, As, Sb (especially fluorides and chlorides) act as Lewis acids and combine with Lewis bases

$$PF_3 + F_2 \longrightarrow PF_5$$
$$SbF_3 + 2F^- \longrightarrow [SbF_5]^{2-}$$

(*b*) **Pentahalides.** Except nitrogen other elements of this group form pentahalides. *Nitrogen cannot form pentahalides because it cannot expand its covalency due to non-availability of d-orbitals in the valence shell.* Phosphorus assumes sp^3d hybridisation and forms five covalent bonds with five chlorine atoms, as shown below :



Some of the characteristics of pentahalides are as follows :

(*i*) The pentahalides in general, have less thermal stability as compared to trihalides.

(*ii*) All the pentahalides act as **Lewis acids.** It is because the central atom can easily accept the halide ions (due to presence of vacant *d*-orbital) and can extend their co-ordination number. Some examples are :

$$PCl_5 + Cl^- \longrightarrow [PCl_6]^-$$
$$SbCl_3 + Cl^- \longrightarrow [SbCl_4]^-$$

It may not be out of place to mention here, that PCl_5 exists as molecule in gaseous state but in solid state it exists as $[PCl_4]^+[PCl_6]^-$ and is ionic in nature. PBr_5, PI_5 also exist in the ionic form in solid state

(*c*) **Oxides.** The elements of this group combine with oxygen directly or indirectly to form a large number of different types of oxides as given in Table 10.11.

Table 10.11. Oxides of Elements of Group 15

Oxidation state of the element	*N*	*P*	*As*	*Sb*	*Bi*
+ 5	N_2O_5	P_4O_{10}	As_2O_5	Sb_2O_5	Bi_2O_5
+ 4	$\begin{bmatrix} N_2O_4 \\ NO_2 \end{bmatrix}$	P_4O_8	—	—	—
+ 3	N_2O_3	P_4O_6	As_2O_3	Sb_2O_3	Bi_2O_3
+ 2	NO	—	—	—	—
+ 1	N_2O	—	—	—	—

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Nature of Oxides

All the oxides of nitrogen (except NO and N_2O) and phosphorus are strongly acidic ; oxides of arsenic are weakly acidic ; oxides of antimony are amphoteric and those of bismuth are weakly basic.

Reason. *The change in character from acidic to basic can be explained on the basis of the size of atoms. As the size of nitrogen atom is small and it has a strong positive field, it interacts with water more strongly pulling the electron pair between O—H bond and thus helps in release of H^+ ions. However, this tendency diminishes with the increase in size and therefore decreases the acidic character or conversely increases the basic character.*

Formation of Oxides

1. The **oxides of nitrogen** can be obtained by the following chemical methods :

(*a*) $$NH_4NO_3 \xrightarrow{\text{heat}} N_2O + 2H_2O$$

(*b*) $$2NaNO_2 + 2FeSO_4 + 3H_2SO_4 \longrightarrow Fe_2(SO_4)_3 + 2NaHSO_4 + 2H_2O + 2NO$$

(*c*) $$2NO + N_2O_4 \xrightarrow{250\ K} 2N_2O_3$$

(*d*) $$2Pb(NO_3)_2 \xrightarrow{673\ K} 4NO_2 + 2PbO + O_2$$

(*e*) $$2NO_2 \underset{\text{heat}}{\overset{\text{cool}}{\rightleftharpoons}} N_2O_4$$

(*f*) $$2HNO_3 + P_2O_5 \longrightarrow 2HPO_3 + N_2O_5$$

The **oxides of P** can be prepared by heating the elements in air.

(*a*) $$P_4 + 3O_2 \xrightarrow{\text{Heat}} P_4O_6$$
(Limited)

(*b*) $$P_4 + 5O_2 \longrightarrow P_4O_{10}$$
(Excess)

The oxides of As (III) and Sb (III) can also be prepared by heating these elements in air.

Structures of oxides

The structure of a few oxides of nitrogen and those of phosphorus are given in Figs. 10.5 and 10.6 respectively.

It is clearly evident from the structures that phosphorus forms cage like structures in its oxides whereas nitrogen does not. It is because P does not enter into $p\pi$—$p\pi$ multiple bonding whereas nitrogen does.

As far as the **stability** of the oxides is concerned, it is found that oxides having elements in the higher oxidation state become less stable as we move down the group. This is because of the inert pair effect.

(*d*) **Oxy acids.** Oxides of N, P and As dissolve in water to form oxy acids. Oxy acids of Sb and Bi are unstable. Some important oxy acids of group 15 elements are listed in Table 10.12.

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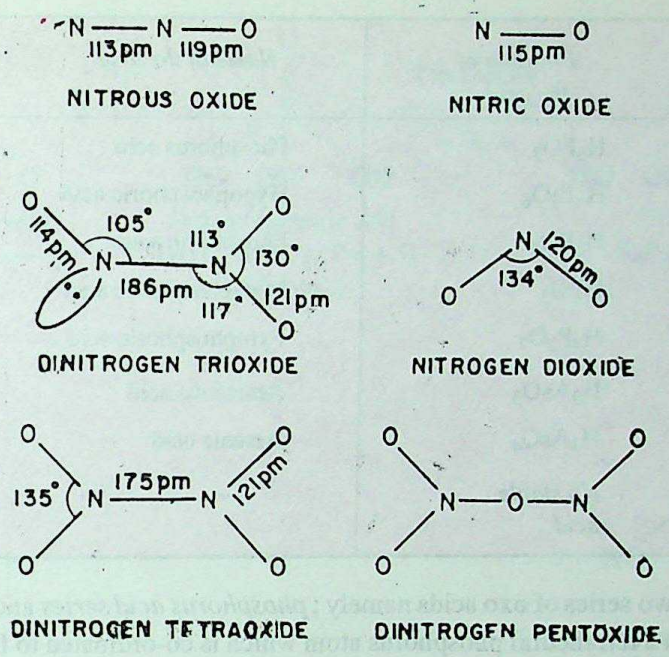

Fig. 10.5. The structure of oxides of nitrogen.

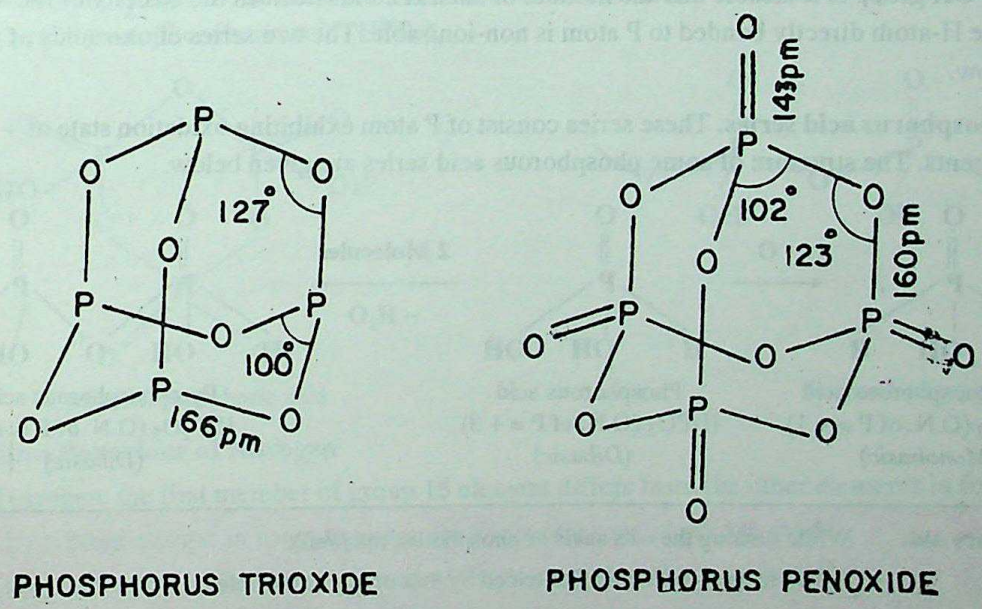

Fig. 10.6. The structures of phosphorus oxides.

Table 10.12. Oxy-acids of Group 15 Elements

Element	*Formula of the acid*	*Name of the acid*	*Oxidation state of the element*
Nitrogen	$H_2N_2O_2$	Hyponitrous acid	+ 1
	$H_4N_2O_4$	Nitroxylic acid	+ 2
	HNO_2	Nitrous acid	+ 3
	HNO_3	Nitric acid	+ 5
	HNO_4	Peroxynitric acid	+ 7

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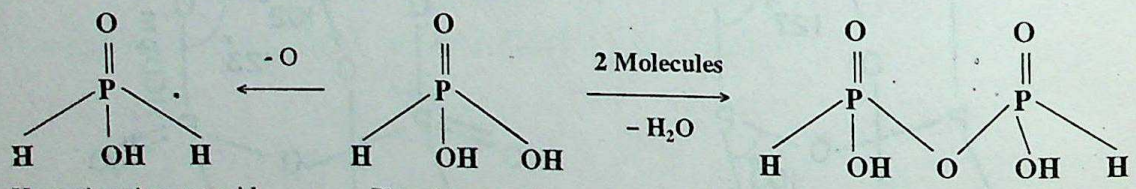
Element	*Formula of the acid*	*Name of the acid*	*Oxidation state of the element*
Phosphorus	H_3PO_3	Phosphorus acid	+ 3
	$H_4P_2O_6$	Hypophosphoric acid	+ 4
	H_3PO_4	Phosphoric acid	+ 5
	HPO_3	Metaphosphoric acid	+ 5
	$H_4P_2O_7$	Pyrophosphoric acid	+ 5
Arsenic	H_3AsO_3	Arsenious acid	+ 3
	H_3AsO_4	Arsenic acid	+ 5
Antimony / **Bismuth**	*No stable acid*	—	—

Phosphorus forms two series of oxo acids namely ; *phosphorus acid series* and *phosphoric acid series*. Each of these series contain a tetrahedral phosphorus atom which is co-ordinated to four atoms. A peculiarity of these oxyacids of phosphorus is that there is at least one P = O unit and P—OH group. In these oxo acids, the H atom of OH group is ionisable and the number of such H atoms decides the basicity of the acid. On the other hand, the H-atom directly bonded to P atom is non-ionisable. The two series of oxo acids of phosphorus are given below.

(*a*) **Phosphorus acid series.** These series consist of P atom exhibiting oxidation state of + 3. They act as reducing agents. The structure of some phosphorous acid series are given below.



Hypophosphorous acid
H_3PO_2 (O.N. of P = + 1)
(*Monobasic*)

Phosphorous acid
H_3PO_3 (O.N. of P = + 3)
(*Dibasic*)

Pyrophosphorous acid
$H_4P_2O_5$ (O.N. of P = + 3)
(*Dibasic*)

Memory aid. While naming the oxo acids of phosphorus, the prefix
- *meta* is used for the acid obtained by loss of H_2O molecule
- *pyro* is used for the acid obtained from two molecules with a loss of H_2O
- *hypo* is used for the acid having lower oxygen content than the parent acid.

(*b*) **Phosphoric acid series.** These series consist of P atom exhibiting oxidation state of + 5. They act as oxidising agents, in general.

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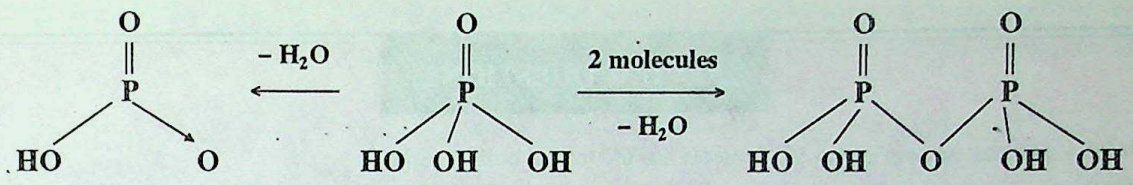
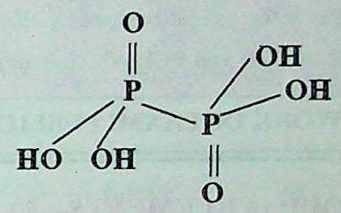


Metaphosphoric acid
HPO_3 (O.N. of P = + 5)
(*Monobasic*)

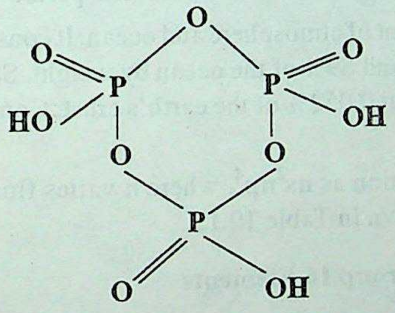
Orthophosphoric acid
H_3PO_4 (O.N. of P = + 5)
(*Tribasic*)

Pyrophosphoric acid
$H_4P_2O_7$ (O.N. of P = + 5)
(*Tetrabasic*)

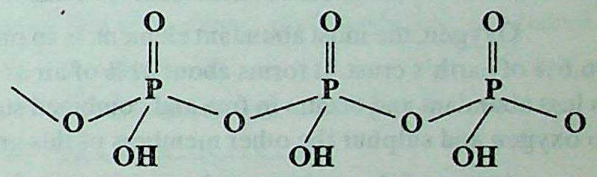


Hypophosphoric acid
$H_4P_2O_5$ (*Tetrabasic*)

*Metaphosphoric acid does not exist in monomeric form, it exists as cyclometaphosphoric acid $(HPO_3)_3$ or polymetaphosphoric acid $(HPO_3)_n$.



Cyclometaphosphoric acid



Polymetaphosphoric acid

Anomalous Behaviour of Nitrogen

Nitrogen, the first member of group 15 element differs from the other elements in following respects.

(*i*) Nitrogen is gas at room temperature while other members are solids.

(*ii*) It does not exhibit penta valency while most of the other elements do

(*iii*) It does not form complexes.

(*iv*) It forms $p\pi$-$p\pi$ bond and exists as N_2 molecule whereas other elements do not have such tendency.

(*v*) It is capable of forming H-bonding while other elements do not form H-bonding.

(*vi*) Nitrogen forms variety of oxides while other elements generally from trioxides and pentoxides only.

The anomalous behaviour of nitrogen is attributed to its :

(*a*) *small size*

(*b*) *high values of ionisation energy and electronegativity and*

(*c*) *non-availability of vacant d-orbitals in the valence shell.*

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REVIEW QUESTIONS

10.37. Which element among group 15 elements has the lowest boiling point ?

10.38. What are the common oxidation states shown by group 15 elements ?

10.39. Among hydrides of group 15 elements which is most basic ?

10.40. How is nitrous oxide (N_2O) prepared ?

10.41. Give electron dot structure of NO_2.

10.42. Name any three oxy-acids of phosphorus.

10.43. What is the oxidation state of nitrogen in nitrous acid ?

10.44. Out of PCl_3 and PCl_5 which is more reactive ?

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10.6. GROUP 16 ELEMENTS—The Oxygen Family

Group 16 of periodic table contains five elements namely, *oxygen* (O), *sulphur* (S), *selenium* (Se), *tellurium* (Te) and *polonium* (Po). These are collectively known as **chalcogens** or ore forming elements because many metal ores occur as oxides and sulphides. These elements belong to *p*-block. The first four members are non-metals. Polonium has metallic character and is a radioactive element with a very short life period.

Oxygen, the most abundant element, is an important constituent of atmosphere and ocean. It constitutes 46.6% of earth's crust. It forms about 21% of air as the free element and 89% of the ocean by weight. Sulphur is less abundant and occurs in free and combined states. It forms about 0.052% of the earth's crust. Compared to oxygen and sulphur the other members of this group are rare.

Atoms of these elements have the outer electronic configuration as $\mathbf{ns^2np^4}$, where *n* varies from 2 to 6. The electronic configurations of the elements of group 16 are shown in Table 10.13.

Table 10.13. Electronic Configurations of Group 16 Elements

Elements	*At. No.*	*Electronic configuration*	*Aboundance in earth's crust (ppm)*
Oxygen (O)	8	[He] $2s^2\,2p^4$	4.66×10^5
Sulphur (S)	16	[Ne] $3s^2\,3p^4$	5.20×10^2
Selenium (Se)	34	[Ar] $3d^{10}\,4s^2\,4p^4$	9.0×10^{-2}
Tellurium (Te)	52	[Kr] $4d^{10}\,5s^2\,5p^4$	2×10^{-3}
Polonium (Po)	84	[Xe] $4f^{14}\,5d^{10}\,6s^2\,6p^4$	—

The four *p*-electrons of the outermost shell are arranged as $px^2\,py^1\,pz^1$. Thus, there are two half-filled *p*-orbitals which are used for bonding with other elements. From the similar outer electronic configuration of these elements, it is expected that they will show similar physical and chemical properties. Some properties of these elements are listed in Table 10.14.

Oxygen the first member of this group has a very high ionisation energy (1314 kJ mol^{-1}) and differs markedly from other members of the family.

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Oxygen, on the other hand, is found to exhibit remarkable resemblance with its neighbours, nitrogen and fluorine. For example, it forms strong $p\pi$-$p\pi$ bond like nitrogen. Also it forms hydrogen bonds like nitrogen and fluorine.

The variation in the properties of various members of the group being described as follows.

General Trends in Physical Properties

1. Density. As expected, the density increases down the group with the increase in atomic number.

2. Melting and Boiling Points. The melting and boiling points show a regular increase down the group.

Reason. *It is because as we move down the group the molecular size increases. As a result, the magnitude of van der Waal forces increase and hence the melting and boiling points also increase.*

3. Ionization energy. These elements possess large values of ionization energies which decrease gradually from O to Po. Oxygen has very high ionization energy (1314 kJ mol^{-1}). The decrease in ionization energy from oxygen to polonium is due to increase in size of the atoms and increase in screening effect of the electrons belonging to lower shells.

4. Metallic and non-metallic character. Metallic character depends on ionization energy. Lesser the ionization energy greater will be the metallic character. As we move down the group, the ionization energy decreases and therefore the metallic character increases. Thus, the first four elements namely oxygen, sulphur, selenium and tellurium are non-metals. The non-metallic character is maximum in O and decreases down the group. Polonium, the last member of the group, is metallic in nature. However, being radio-active it is only short-lived.

5. Catenation. In this group, only S has a strong tendency of catenation. Oxygen also shows this tendency to a limited extent. Thus, the polyoxides and polysulphides of the types, as shown below, are known.

H—O—O—H

Polyoxide

H—S—S—H

H—S—S—S—H

H—S—S—S—S—H

Polysulphides or polysulphanes

Besides these polysulphanes (H—S_n—H), polysulphuric acids HO_3S—S_n—SO_3H, and various allotropic forms of the elements containing different sized S_n rings and chains are also known. The S—S bond is also found in a number of compounds of biological importance such as cysteine, proteins, enzymes, etc.

Table 10.14. Some Properties of Group 16 Elements (Oxygen Family)

Element	*Atomic mass*	*Covalent radius (pm)*	*Ionic radius, M^{-2} (pm)*	*Ionisation energy (kJ mol^{-1})*		*Electronegativity*	*Density*[b]	*Melting point (K)*	*Boiling point (K)*
Oxygen	16.00	74	140	1314.0	3888	3.5	1.32[c]	54	90
Sulphur	32.06	103	184	1000	2251	2.5	2.06[d]	393[f]	718
Selenium,	78.96	119	198	941	2045	2.4	4.19[e]	490	958
Tellurium	127.60	142	221	869	1790	2.1	6.25	725	1260
Polonium	210	168	230[a]	813	—	2.0	—	520	1235

(*a*) approximate value ; (*b*) gm cm^{-3} at 298 K ; (*c*) at the melting point ;
(*d*) rhombic sulphur ; (*e*) hexagonal gray allotrope ; (*f*) monoclinic form.

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6. Oxidation states. All the elements have ns^2np^4 electronic configuration of outermost shell in their atoms. Thus, these tend to acquire the noble gas configuration by sharing or gaining electrons. Oxygen, the first member of the family exhibits the oxidation state of –2 in its compounds owing to its high electronegativity. In addition to the oxidation state of – 2, oxygen also exhibits an oxidation state of – 1 in H_2O_2, zero in O_2 and + 2 in OF_2. Since the electronegativity decreases from oxygen to polonium the tendency to show – 2 oxidation state decreases.

Unlike oxygen, the other elements have a tendency to show + 2, + 4 and + 6 oxidation states. In other words, these elements do not restrict their co-ordination number to two but can exceed this value, *i.e.*, can have a co-ordination number of 4 as well as six in their compounds. This is because of the availability of empty *d*-orbitals in these elements.

7. Multiple Bond Formation. The tendency of these elements to form multiple bonds to carbon and nitrogen decreases as we descend down the group from sulphur to tellurium.

For example, CS_2(S = C = S) is moderately stable, CSe_2 (Se = C = Se) decomposes readily whereas CTe_2 (Te = C = Te) is not known.

8. Electron Affinity. These elements have high electron affinity values which decrease from S to Po. On moving down the group, the size of atom increases and distance of valence shell from nucleus increases. Therefore, additional electron which is added feels lesser attraction as we move down the group and hence electron affinity decreases.

9. Electronegativity. Oxygen is strongly electronegative in character. The value of electronegativity decreases with increase in atomic number down the group. This is due to increase in size of the atoms and decrease in effective nuclear charge as we go down the group.

10. Elemental State. Oxygen exists in a diatonic gaseous state at room temperature while other elements are solids.

Reason. *Due to its small size, oxygen is capable of forming pπ-pπ bond and form O_2 (O = O) molecule. The intermolecular forces in oxygen are weak van der Waal's forces, due to which, it is a gas. The rest of the elements are not able to form pπ- pπ bond due to their large size, and do not exist as M_2 molecules. On the other hand, they exist as puckered rings or chain polymers in which the atoms are linked by covalent bonds. Hence, their boiling points being high, they exist as solids at ordinary temperatures.*

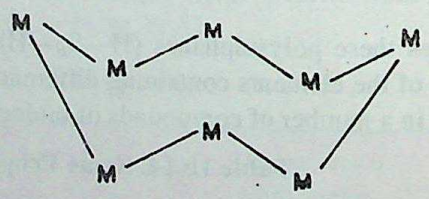

Fig. 10.8. Puckered ring structure of S_8 and Se_8 molecules.

11. Allotropy. All elements of the group exhibit allotropy. Oxygen exists in diatomic (O_2, dioxygen) and triatomic (O_3, ozone) states.

Sulphur is found to exist in several allotropic forms such as rhombic (or α –) sulphur, monoclinic (or β –) sulphur, plastic (or γ –) sulphur and colloidal (or δ –) sulphur. Rhombic and monoclinic sulphur contain S_8 puckered rings and differ only in the packing arrangement. Rhombic sulphur changes to monoclinic above 95.4°C. Plastic sulphur consists of open chains of sulphur atoms. It is prepared by pouring molten sulphur in water.

Selenium has three important allotropes, namely, rhombic, monoclinic and grey forms. The rhombic and monoclinic forms consist of Se_8 molecules. These have puckered ring-like structures as shown in Fig. 10.8.

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The grey form is the most stable form and consists of regularly arranged spirals of selenium atoms. Elemental selenium finds applications in semi-conductor devices as rectifiers.

Chemical Properties

The members of this family show a wide variation in their chemical characteristics. The first member of this group *i.e.*, oxygen mainly forms ionic compounds with metals. This tendency, however, decreases from S to Po due to decrease in electronegativity.

Both O and S are very reactive. In general, the reactivity decreases down the group and oxygen reacts with almost all the elements. Its reactivity is only slightly less than the reactivity of most reactive elements *i.e.*, the halogens (Group 17 elements). Some of the important compounds of this group are discussed below :

1. Hydrides. These elements form volatile hydrides such as H_2O, H_2S, H_2Se, H_2Te and H_2Po.

H_2O may be prepared by burning H_2 in oxygen while other hydrides may be obtained by the action of acids on metal sulphides, selenoids and tellurides, *e.g.*,

$$Na_2S + H_2SO_4 \longrightarrow Na_2SO_4 + H_2S$$

$$Na_2Se + 2HCl \longrightarrow 2NaCl + H_2Se$$

Some important characteristics of these hydrides are discussed below :

(*i*) *Physical nature.* H_2O is colourless, odourless liquid. Other hydrides are colourless poisonous gases with very unpleasant smell. The volatile nature of hydrides first increases from H_2O to H_2S and then decreases. The low volatile character of water is due to the association of water molecules through *hydrogen bonding*. The decrease in volatile nature from H_2S onwards is due to increased interactions among molecules due to increase in molecular size.

(*ii*) *Acidity.* These hydrides are weakly acidic in nature. The acidic nature increases from H_2O to H_2Te. H_2S is a weak diprotic acid which ionizes as :

$$H_2S \rightleftharpoons HS^- + H^+$$

$$HS^- \rightleftharpoons S^{2-} + H^+$$

Reason. *The increase in strength as acid on moving down the group is due to increase in size of the atoms. The distance between central atom and hydrogen increases as we move from O to Te which favours the release of hydrogen as proton. This order of acidity, however, cannot be explained in terms electronegativity of these elements. The acidic character thus follows the order*

$$H_2O < H_2S < H_2Se < H_2Te$$

The values of dissociation constants (K_a) of these compounds are given below.

Hydride	H_2O	H_2S	H_2Se	H_2Te
K_a *Value*	1×10^{-14}	1×10^{-7}	1.7×10^{-4}	2.3×10^{-2}

(*iii*) *Reducing character.* All the hydrides, except water, are reducing agents. The reducing character increases on moving from H_2S to H_2Te. *This is presumably due to the increase in the size of the central atom due to which the strength of M—H bond and also the stability decreases down the group.*

A comparative study of some of these properties are listed in Table 10.5.

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Table 10.15. Some Physical Properties of Hydrides of Group 16 Elements

Hydride	*Melting point (K)*	*Boiling point (K)*	*M – H distance (pm)*	*HMH angle (degrees)*	$\Delta H°$ ($kJ\ mol^{-1}$)	ΔH_{M-H} ($kJ\ mol^{-1}$)
H_2O	273	373	96	104	– 286	463
H_2S	188	213	134	92	20	347
H_2Se	208	232	146	91	73	276
H_2Te	222	269	169	90	100	278
	DECREASE	DECREASE	INCREASE	DECREASE		DECREASE
	INCREASE	INCREASE				

2. Halides. The elements of group 16 form a number of halides. The more important halides being hexa-, tetra- and dihalides and are given in Table 10.16.

Table 10.16. Some Important Halides of Group 16 Elements

Element	*Fluorides*	*Chlorides*	*Bromides*	*Iodides*
O	OF_2	Cl_2O, ClO_2, Cl_2O_7	Br_2O	I_2O_5
S	S_2F_2, SF_4, SF_6	S_2Cl_2, SCl_2	S_2Br_3	—
Se	Se_2F_2, SeF_4, SeF_6	Se_2Cl_2, $SeCl_4$	$SeBr_2$, $SeBr_4$	—
Te	TeF_4, TeF_6	$TeCl_2$, $TeCl_4$	$TeBr_2$, $TeBr_4$	TeI_4
Po	—	$PoCl_2$, $PoCl_4$	$PoBr_2$, $PoBr_4$	PoI_4

(*i*) The compounds of fluorine with oxygen are called *fluorides*, therefore, F_2O is more correctly written as OF_2 and called oxygen difluoride. As Cl, Br and I are less electronegative than oxygen, therefore, compounds of these halogens with oxygen are called *oxides e.g.*, ClO_2, I_2O_5, Cl_2O_7 are respectively called chlorine dioxide, iodine pentaoxide and chlorine heptoxide respectively.

(*ii*) Sulphur forms a number of halides of the type S_2X_2 (X = F, Cl, Br, I), SX_2 (X = F, Cl Br), SX_4 (X = F, Cl) and SX_6 (X = F). Selenium and tellurium also form chlorides and bromides in oxidation states of + 1, + 2, + 4 and + 6.

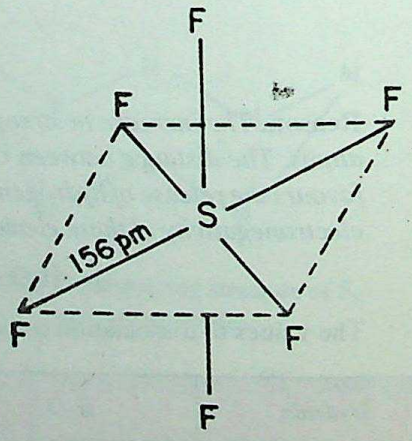

Fig. 10.9 (*a*)

Structure of halides

(*a*) The hexafluorides of S, Se and Te *i.e.*, SF_6, SeF_6, TeF_6 have the central atom in sp^3d^2 hybridised state. These fluorides have octahedral structure. It is the small size of fluorine which brings out the maximum covalency. It may be noted that hexahalides with Cl, Br and I are not formed. Due to the bigger size of these halogen atoms a co-ordination number of six is not achieved.

(*b*) Amongst the tetrafluorides of S, Se and Te, SF_4 is gaseous, SeF_4 is liquid and TeF_4 is solid. The tetrachloride of S, SCl_4 is an unstable liquid while other tetrachlorides are solids.

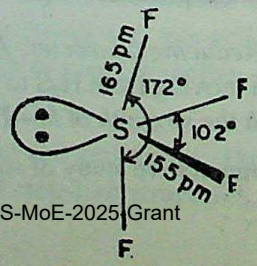

Fig. 10.9 (*b*)

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In tetrahalides sp^3d hybridisation occurs and thus these have got a trigonal bipyramidal structure with one of the equatorial position occupied by a lone pair of electron. The structure of SF_4 is shown in Fig. 10.9 (*b*).

3. Oxides. The elements of this group form a number of oxides. Some of the oxides formed by these elements are listed in the Table 10.17.

(*i*) All elements (except Se) form monoxide.

(*ii*) All elements form dioxide with formula $\mathbf{MO_2}$. SO_2 is a gas, SeO_2 is a volatile solid while TeO_2 and PoO_2 are non-volatile crystalline solids.

Table 10.17. Oxides of S, Se, Te and Po

Elements	*Monoxide*	*Dioxide*	*Trioxide*
Sulphur	SO	SO_2	SO_3
Selenium	—	SeO_2	SeO_3
Tellurium	TeO	TeO_2	TeO_3
Polonium	PoO	PoO_2	—

The SO_2 molecule is a hybrid of the two resonating forms and has a bent structure with bond angle of 119° around S as shown below is Fig. 10.10 (*a*). Selenium and tellurium dioxides are solids having polymeric chain as shown in Fig. 10.10 (*b*).

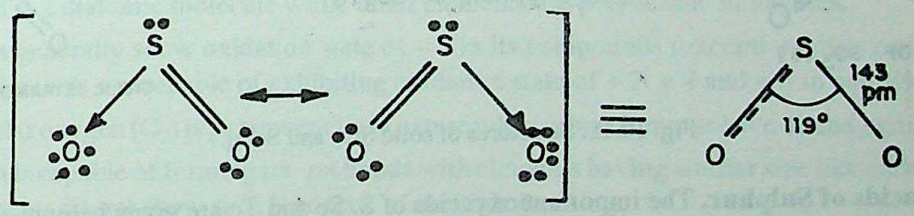

Fig. 10.10. (*a*) Structure of SO_2.

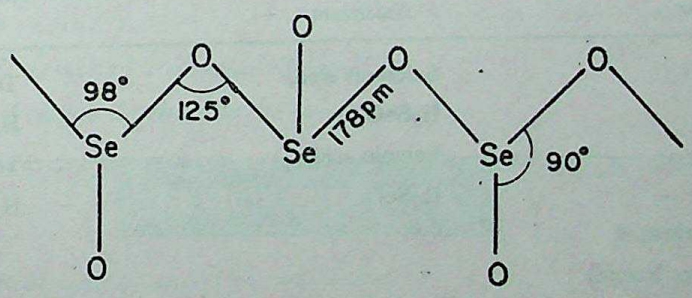

Fig. 10.10. (*b*) Chain structure of SeO_2 in solid state.

The acidic character of the dioxides **decreases** as we move down the group.

(*iii*) All the group 16 elements form the trioxides, $\mathbf{MO_3}$. The best known trioxide is SO_3. It is obtained by the catalytic oxidation of sulphur dioxide.

$$SO_2 + \frac{1}{2}O_2 \xrightarrow[625\ K]{V_2O_5} SO_3$$

SO_3 molecule is a hybrid of three resonating forms and possesses a trigonal planar structure in gaseous state as shown on the next page :

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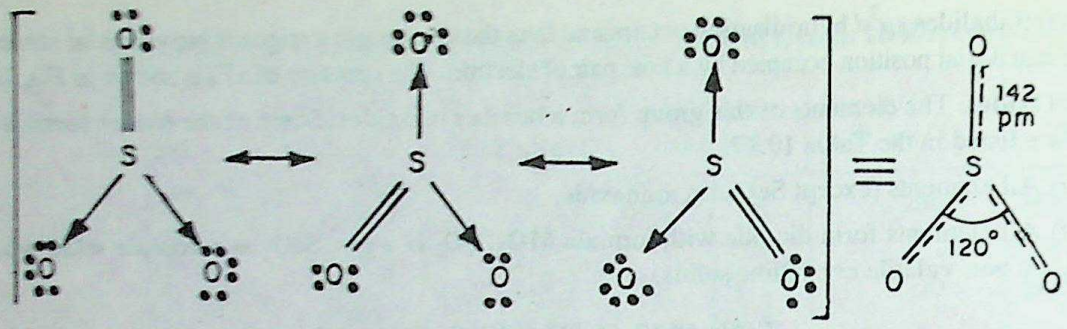

In solid state it can exist either as a cyclic trimer, $(SO_3)_3$ or as a linear chain cross-linked into sheets. Selenium trioxide solid is a cyclic tetramer whereas TeO_2 is a solid with network structure.

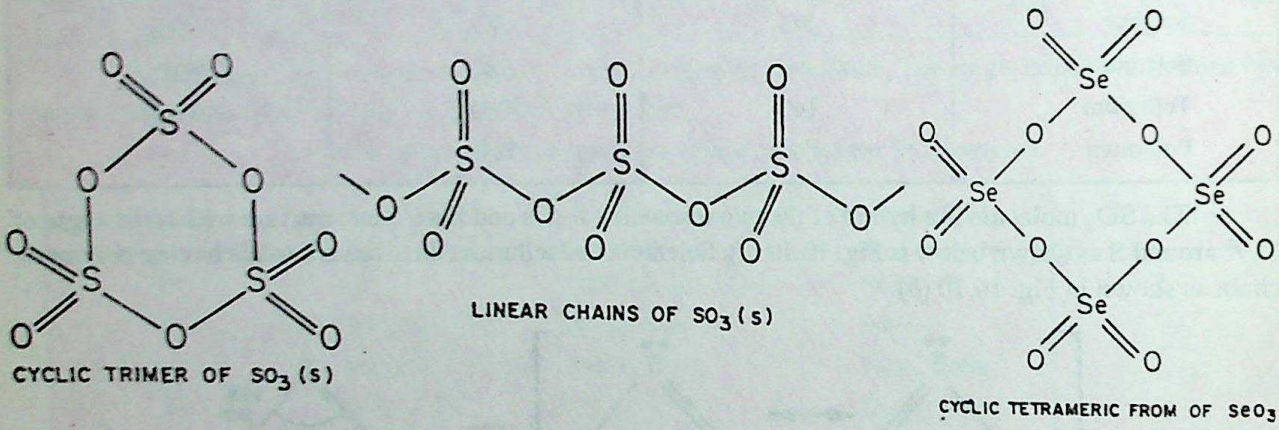

Fig. 10.11. Structures of solid SO_3 and SeO_3.

(*d*) **Oxyacids of Sulphur.** The important oxyacids of S, Se and Te are given below :

Sulphur	*Selenium*	*Tellurium*
Sulphurous acid, H_2SO_3	Selenous acid, H_2SeO_3	Tellurous acid, H_2TeO_3
Sulphuric acid, H_2SO_4	Selenic acid, H_2SeO_4	Telluric acid, H_2TeO_4
Peroxomonosulphuric acid, H_2SO_5 (*Caro's acid*)		
Peroxodisulphuric acid, $H_2S_2O_8$ (*Marshell's acid*)		
Thiosulphuric acid, $H_2S_2O_3$		
Dithionic acid, $H_2S_2O_6$		
Pyrosulphuric acid, $H_2S_2O_7$		

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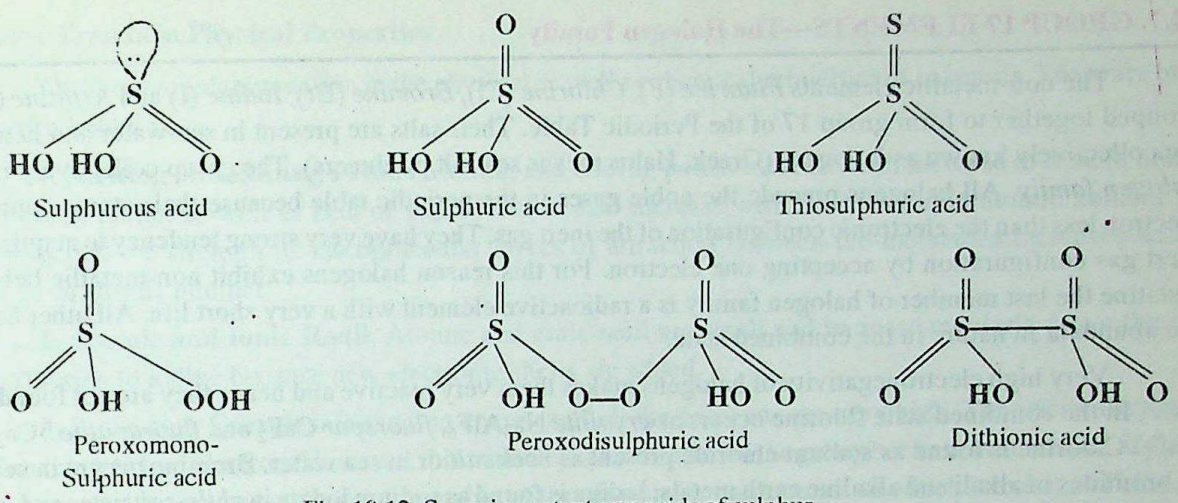

Fig. 10.12. Some important oxy acids of sulphur.

The oxy acids of sulphur are more numerous and important than those of Se and Te. The structures of some of the principal acids formed by sulphur are shown in Fig. 10.12.

Anamolous Behaviour of Oxygen

Oxygen differs from the rest of the elements in the family in the following respects,

(*i*) Oxygen is gas at ordinary temperature whereas other elements are solids.

(*ii*) Oxygen is a diatomic molecule while other elements are polyatomic molecules.

(*iii*) Oxygen generally show oxidation state of – 2 in its compounds (exceptions being peroxides and OF_2) while other elements are capable of exhibiting oxidation state of + 2, + 4 and + 6 in addition to – 2.

(*iv*) Molecular oxygen (O_2) is paramagnetic in nature while other elements have diamagnetic behaviour.

(*v*) Oxygen is capable of forming $p\pi$- $p\pi$ bonds with elements having similar size like carbon, nitrogen etc., but other elements do not show such tendency of multiple bonding.

The anomalous behaviour of oxygen is attributed to its :

(*a*) *small size,*

(*b*) *high values of I.E. as well electronegativity and*

(*c*) *non-availability of vacant d-orbital in the valence shell.*

REVIEW QUESTIONS

10.45. Name the most abundant element present in the earth's crust.

10.46. Which element of group 16 shows catenation to maximum extent ?

10.47. Among the group 16 elements which element has lowest melting and boiling points.

10.48. Among hydrides of chalcogens which is most acidic and which is most stable ?

10.49. What is the state of hybridisation of sulphur in

(*i*) SF_6 (*ii*) SF_4 (*iii*) SO_3.

10.50. Name any two oxy-acids of sulphur and indicate the oxidation state of sulphur in them.

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10.7. GROUP 17 ELEMENTS—The Halogen Family

The non-metallic elements *Fluorine* (F), *Chlorine* (Cl), *Bromine* (Br), *Iodine* (I) and *Astatine* (At) are grouped together to form group 17 of the Periodic Table. Their salts are present in sea-water and hence they are collectively known as *halogens* (Greek, Halos means sea salt producers). The group collectively is called *halogen family*. All halogens precede the noble gases in the periodic table because their atoms contain one electron less than the electronic configuration of the inert gas. They have very strong tendency to acquire stable inert gas configuration by accepting one electron. For this reason halogens exhibit non-metallic behaviour. Astatine the last member of halogen family is a radioactive element with a very short life. All other halogens are abundant in nature in the combined state.

Very high electronegativity of halogens makes them very reactive and hence they are not found in free state. In the combined state fluorine occurs as *cryollite* Na_3AlF_6, *fluorspar* CaF_2 and *fluorapatite* $3Ca_3(PO_4)_2 CaF_2$. Chlorine is found as sodium chloride present as *rock salt* or in sea water. Bromine occurs in sea water as bromides of alkali and alkaline earth metals. Iodine is found as sodium iodate in *chile-salt petre* and as alkali metal iodides and alkaline earth metal iodides in sea water.

The general electronic configuration of halogens is $\mathbf{ns^2np^5}$.

The electronic configurations of halogens are given in Table 10.18.

Table 10.18. Electronic Configuration of Halogens

Elements	*At. No.*	*Electronic configuration*	*Abundance in earth's crust (ppm)*
Fluorine (F)	9	[He] $2s^2 2p^5$	800
Chlorine (Cl)	17	[Ne] $3s^2 3p^5$	480
Bromine (Br)	35	[Ar] $3d^{10} 4s^2 4p^5$	2
Iodine (I)	53	[Kr] $4d^{10} 5s^2 5p^5$	0.3
Astatine (At)	85	[Xe] $4f^{14} 5d^{10} 6s^2 6p^5$	—

Halogens exist in the elemental form as diatomic molecule having characteristic colours. Fluorine exhibits only negative oxidation state of – 1. Other halogens in addition to – 1 oxidation state exhibit formal positive oxidation states.

Some of the properties of group 17 elements are given in Table 10.19.

Table 10.19. Some Properties of Group 17 Elements

Element	*Atomic mass*	*Covalent radius (pm)*	*Ionic radius X^- (pm)*	*Ionisation energy (kJ cm^{-3})*	*Electro-negati-vity*	*Density (g cm^{-3})^a*	*Melting point (K)*	*Boiling point (K)*	*Distance X—X in X_2 (pm)*	*Heat of dissociation $X_2(s) \rightarrow 2X$ (kJ mol^{-1})*
Fluorine	19.00	72	133	1680	4	1.51 (85)	54.4	84.9	143	158.8
Chlorine	35.45	99	184	1256	3.2	1.66 (203)	172	239	199	242.6
Bromine	79.90	114	196	1142	3.0	3.19 (273)	265.8	332.5	228	192.8
Iodine	126.90	113	220	1008	2.7	3.96 (393)	386.6	458.2	266	151.1
Astatine^b	210.00	—	—	—	2.2	—	—	—	—	—

(*a*) For the liquid at temperature (K) given in parenthesis, (*b*) Radioactive.

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General Trends in Physical Properties

There is a regular gradation in the physical as well as chemical properties of halogens. These are briefly discussed below :

1. Melting and Boiling Points. Melting and boiling points increase with increase in atomic number. The heat of fusion as well as heat of vapourisation also increase with the increase in atomic number. This indicates that the strength of intermolecular forces of attraction between the molecules increases with the increase in atomic number.

2. Atomic and Ionic Radii. Atomic and ionic radii are small and increase regularly down the group from fluorine to iodine because new electronic shells are added.

3. Ionization Energies. Ionization energies of all the halogens are very high. Therefore, they have a less tendency to lose electron. However, this tendency increases down the group because the distance of valence shell from nucleus increases. Iodine is capable of forming stable compounds in which it exists as I^+ ion.

4. Physical Sate. The halogens are all diatomic and exist as F_2, Cl_2, Br_2 and I_2. The intermolecular forces are very weak in halogens. The nature of forces is van der Waal's and their magnitude increases down the group.

Thus, F_2 and Cl_2 are gases, bromine is a volatile liquid and iodine is a volatile solid.

5. Colour. Halogens are coloured.

The colour of different halogens are as follows :

Halogen	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
Colour	Pale yellow	Greenish yellow	Reddish brown	Dark violet

Reason. *The colour of the halogen is due to absorption of visible light by their molecules resulting in the excitation of outer electron to higher energy levels. Fluorine being smaller in size absorbs violet light (of high energy) for excitation and appears pale yellow while iodine absorbs yellow light (of less energy) for excitation and therefore appears violet black. In between, the colour of chlorine is yellowish-green and of bromine is reddish-brown or orange. Thus, the colour deepens down the group.*

6. Non-metallic character. All the halogens have very high values of ionization energies and exhibit non-metallic character. The non-metallic character, however, decreases down the group. Iodine shows some distinct metallic properties *e.g.*, it possesses metallic lustre and forms positive ions like I^+, I^{3+} etc.

7. Electron affinities. Since halogens have strong tendency to accept electrons, they have high values of electron affinities. On moving down the group electron affinity values decrease because size of the atom increases. However, it has been observed that fluorine has less electron affinity than chlorine. *A low value of electron affinity for fluorine is due to the small size of fluorine atom. In a compact 2p sub-shell of fluorine the added electron does not feel much attraction resulting in low value of electron affinity.*

8. Oxidation states. All the elements of the halogen family have a tendency to acquire noble gas electronic configuration by either accepting an electron resulting in the formation of monovalent anion or by sharing one electron with those of other elements. Thus, they show an oxidation state of – 1 or + 1 depending on whether the element combining with halogens is less electro-negative or more electronegative than halogen. Since fluorine is most electronegative element it always has – 1 oxidation state and never has a positive oxidation state. Also higher oxidation states are not possible in fluorine as it does not have vacant *d*-orbitals.

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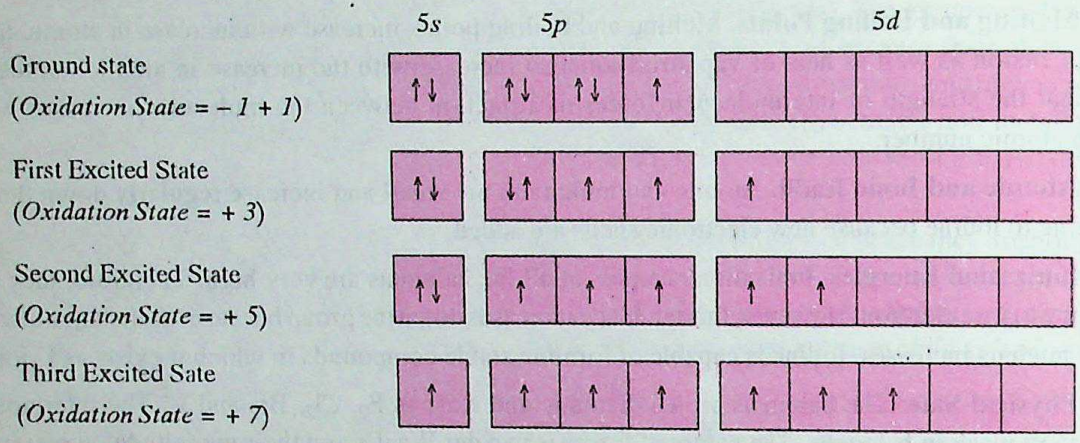
Other elements of this group show oxidation states of + 1, + 3, + 5 and + 7 in addition to – 1 state which is most common. Higher oxidation states of these elements are due to the presence of vacant *d*-orbitals. The outer *s* or *p* electrons can easily be excited to these vacant *d*-orbitals as shown below in case of iodine.



9. Nature of bonds with other elements. The halogens combine with metals to form predominantly ionic halides. The ionic character of these halides decreases while covalent character increases on going down the halogen group. This is due to the reason that with increase in size of the halide ion, its polarizability increases and this imparts covalent character to the compound. For example, AlF_3 is predominantly ionic whereas $AlCl_3$ and $AlBr_3$ are predominantly covalent.

With metals in higher oxidation states or with non-metals, halogens form covalent compounds which are polar in character. Polarity of these compounds decreases as we move down the group.

Chemical Properties

All the halogens are very reactive but amongst them fluorine is the most reactive. As we move down the group, reactivity decreases. This is due to the decrease in electronegativity and increase in bond dissociation energy. In general, a halogen of low atomic number oxidises halide ions of higher atomic number *i.e.*, F_2 displaces Cl_2, Br_2 and I_2 from their salts, Cl_2 displaces Br_2 and I_2 whereas Br_2 displaces iodine from its salts, *e.g.*,

$$F_2 + 2X^- \longrightarrow 2F^- + X_2 \qquad (X = Cl, Br, I)$$

$$F_2 + 2KX \longrightarrow 2KF + X_2 \qquad (X = Cl, Br, I)$$

$$Cl_2 + 2X^- \longrightarrow 2Cl^- + X_2 \qquad (X = Br, I)$$

$$Br_2 + 2I^- \longrightarrow 2Br^- + I_2$$

1. Oxidising power. The halogens act as strong oxidising agents. It is because of their high electron affinities that they have great tendency to take up electrons. The oxidising power of the halogens decreases on going down the group from fluorine to astatine. The decrease in the value of their reduction potentials, as shown below, support the above fact.

X_2	F_2	Cl_2	Br_2	I_2	At_2
E° (Volts)*	2.87	1.40	1.09	0.62	~ 0.3

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Here, a curious question may arise in the minds of the students that why fluorine is a better oxidising agent then chlorine although its electron affinity is less than that of chlorine. In fact, E° values of halogens refer to the process

$$\frac{1}{2}X_2(g) + \bar{e} + aq \longrightarrow \bar{X}(eq)$$

which comprises of the following sequence of steps.

(*i*) **Dissociation**

$$\frac{1}{2}X_2(g) \longrightarrow X(g)\ ;\ \frac{1}{2}\Delta H_{Dissociation} = +\text{ve}$$

(*ii*) **Accepting the electron**

$$X(g) + \bar{e} \longrightarrow \bar{X}(g)\ ;\ \Delta H = -\text{ve}$$

(*iii*) **Hydration of anion**

$$\bar{X}(g) + aq \longrightarrow \bar{X}(aq)\ ;\ \Delta H_{Hydration} = -\text{ve}$$

Now, $\Delta H_{Dissociation}$ of $F_2(g)$ (79.1 kJ) is smaller than that of Cl_2 (122 kJ). Electron affinity of Cl (– 384 kJ) is higher than that of F (– 333 kJ). The value of $\Delta H_{Hydration}$ of $\bar{F}$ ion (– 460 kJ) is much higher than that of $\bar{Cl}$ ion (– 383 kJ). It is due to small size and high charge density of $\bar{F}$ ion. Thus, net energy released for $\frac{1}{2}F_2(g) \longrightarrow \bar{F}(aq)$ is – 752 kJ whereas that for $\frac{1}{2}Cl_2(g) \longrightarrow Cl^-(aq)$ is – 708 kJ, which accounts for higher oxidising power of F_2.

2. Hydrides. Halogens combine with hydrogen to form volatile halides of the formula HX. Some characteristics of these hydrides are given below :

(*i*) *Physical Nature.* Except HF, all other hydrides *viz.*, HCl, HBr and HI are gases. HF is a liquid because of *intermolecular hydrogen bonding.*

—H—F....H—F....H—F....

The bond between hydrogen and halogen is covalent in all the cases.

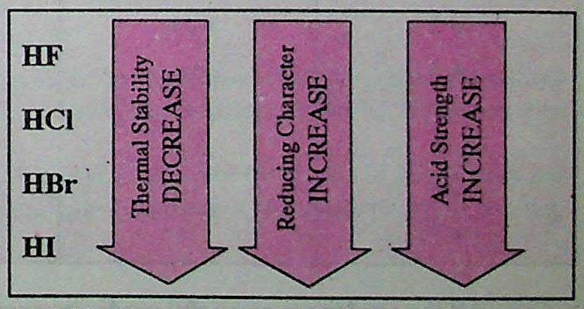
(*ii*) *Acidic Strength.* All the hydrogen halides act as acids in their aqueous solutions. The acidic strength varies in the order

HF < HCl < HBr < HI

Reason. *All the halogen acids ionise to give H^+ ion and halide ion, X^-.*

$HX \longrightarrow H^+ + X^-$; (where $X^- = F^-, Cl^-, Br^-, I^-$)

The above order of acidic character can be explained in terms of strength of H—X bonds, which is in the order H—I < H—Br < H—Cl < H—F. Since H—I bond is weakest, therefore, ***HI is the strongest acid.*** *On the other hand H—F bond is strongest, hence it is the weakest acid among all the halogen acids.*



(*iii*) *Reducing Character.* The reducing character of the hydrides increases down the group. It is because the strength of H—X bond decreases from HF to HI. Lower is the strength of bond greater is the ease with which it can be cleaved and hence greater is the reducing character.

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3. Halides. The halogens, in general, react with almost all the metals and non-metals except He, Ne and Ar to form a wide variety of binary halides. These may either be simple or complex molecules which differ from each other in their stoichiometries and hence in structures, as well.

(*i*) With metals like Na, K, Mg, etc. having low ionisation energies, the halogens react to form ionic halides which have got high boiling and melting points. As the electronegativity of the halogens decreases down the group the ionic character decreases in the order :

$$M—F > M—Cl > M—Br > M—I$$

(*ii*) With metals having high ionisation energies, *e.g.*, Sn, Pb, Sb, etc. the halogens form covalent halides. The halides of these metals in higher oxidation states, *e.g.*, $SnCl_4$, $PbCl_4$, $SbCl_5$, etc. are more covalent than the halides in lower oxidation states, *i.e.* $SnCl_2$, $PbCl_2$, $SbCl_3$ etc.

(*iii*) With non-metals like P, As, S the halogens readily form covalent halides such as PF_5, PCl_3, PBr_3, $AsCl_3$, S_2Cl_2, etc.

4. Oxides. Halogens do not combine with oxygen directly but their oxides with oxygen can be prepared indirectly. For example, oxygen difluoride, OF_2 is prepared by the action of fluorine on 2% sodium hydroxide solution.

$$2F_2 + 2NaOH \longrightarrow 2NaF + OF_2 + H_2O$$

Similarly, dichlorine oxide, Cl_2O is obtained indirectly by passing chlorine over precipitated mercuric oxide.

$$2Cl_2 + 2HgO \xrightarrow{575\ K} HgO.HgCl_2 + Cl_2O$$

The compounds of oxygen with fluorine are called as fluorides because fluorine is more electronegative then oxygen. Most of these compounds are endothermic and unstable and are likely to explode resulting in the formation of more stable products. Among oxides of each halogen the higher oxides are relatively more stable. Some of these oxides are given below in Table 10.20.

Table 10.20. Oxides of Halogens

Oxidation state	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
+ 1	OF_2	Cl_2O	Br_2O	—
+ 2	F_2O_2			
+ 3	—	Cl_2O_3		
+ 4	—	ClO_2	BrO_2	I_2O_4
+ 5	—	—	—	I_2O_5
+ 6	—	Cl_2O_6	—	—
+ 7	—	Cl_2O_7	—	—

All the oxides are powerful oxidising agents and decompose explositively when subjected to mechanical shock or heat.

The structure and molecular dimensions of some of the oxides are shown below :

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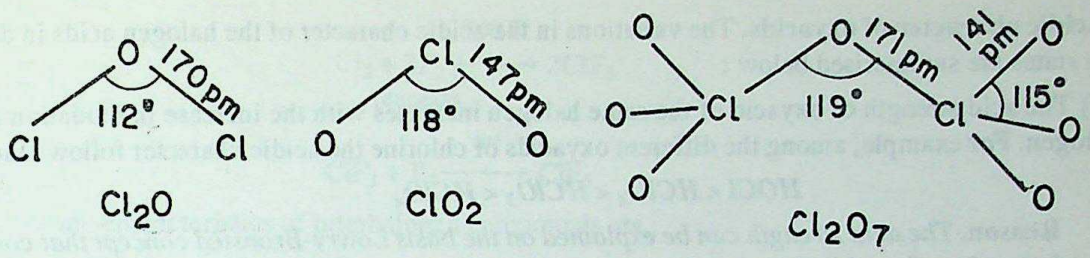


5. Oxyacids. Fluorine yields only one oxyacid, hypofluorous acid (HOF). Chlorine, bromine and iodine form four series of acids with formulae : HOX, HXO_2, HXO_3 and HXO_4, although many of these are known only in solutions or as salts.

Various Oxoacids of Halogens are given below in Table 10.21.

Table 10.21. Oxoacids of halogens

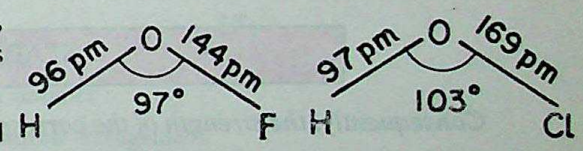
	Oxidation state	*Fluorine*	*Chlorine*	*Bromine*	*Iodine*
Hypohalous acids	+ 1	HOF	HOCl	HOBr	HOI
Halous acids	+ 3	—	$HClO_2$	—	—
Halic acids	+ 5	—	$HClO_3$	$HBrO_3$	HIO_3
Perhalic acids	+ 7	—	$HClO_4$	$HBrO_4$	HIO_4

(*i*) The **Hypohalous acids** HOCl, HOBr and HOI are weak acids and are only formed in aqueous solutions by disproportionation of the halogen water

$$X_2 + H_2O \rightleftharpoons HOX + HX \qquad (X = Cl, Br, I)$$

Salts of these acids are known as hypohalites, *e.g.*, bleaching powder, $CaOCl_2$ is a common example of this category.

The structures of HOCl and HOF alongwith structural parameters are shown below :



(*ii*) The **halic acids** $HClO_3$ and $HBrO_3$ are also known in solutions, but iodic acid HIO_3 exists as a white solid. Thus, the stability of acids increases with increase in atomic number of the halogen. These acids act as **strong oxidising agents,** *e.g.*, these oxidise halides to give halogens in acid medium.

$$OX_3^- + 5X^- + 6H^+ \longrightarrow 3X_2 + 3H_2O$$

The salts of these are called **halates.** Amongst the halates, sodium chlorate ($NaClO_3$) and potassium chlorate ($KClO_3$) are prepared on industrial scale. $NaClO_3$ is a powerful weed killer, whilst $KClO_3$ is used in fireworks and matches.

(*iii*) **Perhalic acid** *i.e.*, perchloric, periodic acids as well as their salts perchlorates and periodates are known to exist. The perhalates (MXO_4) are prepared by the electrolytic oxidation of the corresponding halates, MXO_3.

$$4ClO_3^- \longrightarrow Cl^- + 3ClO_4^-$$

The disproportionation of BrO_3^- to BrO_4^- is unfavourable, therefore per bromates are obtained only by oxidation of BrO_3^- by F_2 in basic solution.

$$BrO_3^- + F_2 + 2OH^- \longrightarrow BrO_4^- + 2F^- + H_2O$$

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Acidic character of oxyacids. The variations in the acidic character of the halogen acids in different oxidation states are summarised below :

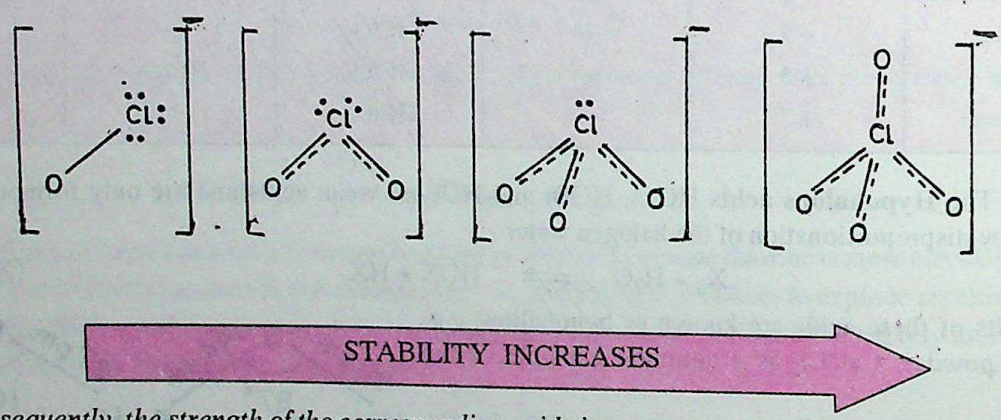
(*i*) The acid strength of oxyacid of the same halogen increases with the increase in oxidation number of the halogen. For example, among the different oxyacids of chlorine the acidic character follows the order

$$HOCl < HClO_2 < HClO_3 < HClO_4$$

Reason. *The acid strength can be explained on the basis Lowry-Bronsted concept that* ***conjugate base of weak acid is strong and conjugate base of strong acid is weaker.***

$$\underset{Acid_1}{HA} + H_2O \rightleftharpoons H_3O^+ + \underset{Conjugate\ Base_1}{A^-}$$

Now greater is the stability of A^-, lesser will be its basic strength or greater will be the tendency of HA to release H^+. In other words, stronger will be the acid HA. Among the conjugate bases of the oxoacids i.e., ClO^-, ClO_2^-, ClO_3^- and ClO_4^-, the stability increases with increase in the number of oxygen atom in the anion. It is because, more is the number of oxygen atoms in the ion, greater will be the dispersal of negative charge and thus, more will be its stability.



Consequently, the strength of the corresponding acids increases as

$$HOCl < HClO_2 < HClO_3 < HClO_4$$

(*ii*) Among the oxyacids of different halogens having the same oxidation number, the acidic character decreases with the increase in atomic number. For example, the decreasing acidic character among hypohalous series is

$$HClO > HBrO > HIO.$$

Reason. *Greater is the size of the halogen atom lesser will be its electronegativity and hence lesser shall be the acidic character.*

6. Interhalogen Compounds

Halogens are known to form compounds by combining among themselves. These are known as interhalogen compounds. In short, the interhalogen compounds may be defined as the ***compounds containing two or more halogen atoms in their molecules.*** These are divided into four types *i.e.* AX (ClF, BrF, BrCl, ICl, IBr) ; AX_3 (ClF_3, BrF_3, ICl_3) ; AX_5 (BrF_5, IF_5) and AX_7 (IF_7).

All these can be prepared by direct combination or by the action of a halogen on a lower interhalogen. The product formed depends on the conditions. For example,

$$\underset{(1:1)}{Cl_2 + F_2} \xrightarrow{500\ K} 2ClF$$

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$$Cl_2 + \underset{\text{(excess)}}{3F_2} \xrightarrow{500\ K} 2ClF_3$$

$$ClF_3 + F_2 \xrightarrow{h\nu} ClF_5$$

Some characteristics of interhalogen compounds are :

(*i*) They are covalent compounds.

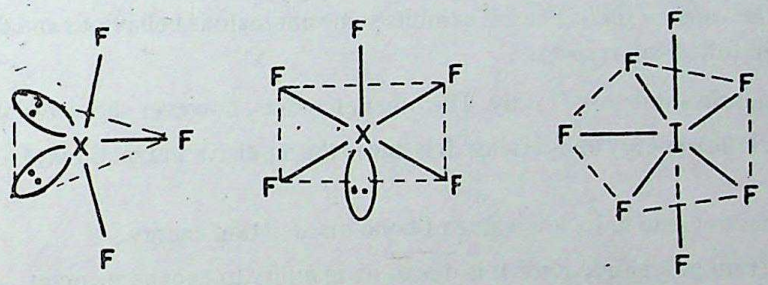
(*ii*) *They are more reactive than the constituent halogens. It is because A—X bond is relatively weaker than X—X bond.*

(*iii*) They are very good oxidising agents.

(*iv*) Their melting and boiling points increase with the increase in the difference of electronegativity.

Structure of interhalogen compounds

The molecular structure of interhalogen compounds can be explained on the basis of VSEPR theory. The structures of a few interhalogens are shown below :



X = Cl, Br, I X = Cl, Br, I IF_7

It may be noted than in general, the central halogen atom assumes :

- *sp^3d hybridisation* in AX_3 which has a trigonal bipyramidal arrangement.
- *sp^3d^2 hybridisation* in AX_5 which has octahedral arrangement.
- *sp^3d^3 hybridisation* in AX_7 which has pentagonal bipyramidal arrangement.

Polyhalide ions

In addition to neutral interhalogen compounds polyhalide ions containing more than two halogen atoms have also been prepared. These are formed by the combination between the halide ion with another halogen atom or with some compound of halogen. For example, I_3^- (triodide/ion is formed by combination of I_2 molecule and iodide ion (I^-).

$$I^-(aq) + I_2 \rightleftharpoons I_3^-(aq)$$

Some other examples of polyhalide anions are ICl_2^-, IBr_2^-, ICl_4^-, BrF_4^-, IF_6^-, etc. Besides anions, I_3^+ is a common example of ***polyhalide cation.*** This ion is found to exist in compounds like iodine triacetate, $I(CH_3COO)_3$ iodine phosphate (IPO_4) and iodine perchlorate, $I(ClO_4)_3$.

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Pseudo halide ions

Certain uninegative ions which are made of two or more electronegative atoms of which one is at least N atom possess properties similar to halide ions. They are called pseudo halide ions. They form salt similar to halide ions. The corresponding covalent dimers of pseudo halide ions are called **pseudo halogens.** Some examples are given below :

Pseudo halide ions	Pseudo halogens
CN^- Cyanide	$(CN)_2$ Cyanogen
SCN^- Thiocyanate	$(SCN)_2$ Thiocyanogen
OCN^- Cyanate	$(OCN)_2$ Oxycyanogen
$SeCN^-$ Selenocyanide	$(SeCN)_2$ Selenocynogen
OCN^- Isocyanate or fulminate	
NCN^- Cyanamide	
N_3^- Azide	

Anomalous Behaviour of Fluorine

Fluorine has *extremely small size, high electronegativity, high ionisation potential and no availability of vacant d-orbitals in the valence shell.* Thus, it exhibits some anomalous behaviour and differs from the other elements of the group in following respects :

(*i*) It shows oxidation state of – 1 only. The other elements, however show variable oxidation states.

(*ii*) Bond dissociation energy of F_2 is least. It is due to the repulsive interactions of lone pairs of electrons around F atoms.

(*iii*) It is most reactive due to its low value of bond dissociation energy.

(*iv*) It does not from polyhalide ions. It is due to its inability to expand its octet.

(*v*) The hydride of fluorine (HF) is liquid (*due to intermolecular H-bonds*) at room temperature where as hydrides of other elements of the group are gases.

(*vi*) The compounds of fluorine have maximum ionic character.

REVIEW QUESTIONS

10.51. How do melting points change with increase in atomic number among group-17 elements ?

10.52. On the basis of general trend what is the expected physical state of At_2 at room temperature ?

10.53. Among halogens

(*i*) Which element is most electronegative ? (*ii*) Which element has highest E.A. ?

(*iii*) Which element has lowest boiling point ?

10.54. Name the strongest oxidising agent among all the elements.

10.55. Among hydrides of halogens

(*i*) which is most stable ? (*ii*) which is most acidic ?

(*iii*) which has lowest boiling point ?

10.56. What is the state of hybridisation of Br in (*i*) BrF_3, (*ii*) BrF_5 ?

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10.8. GROUP 18 ELEMENTS—The Noble Gases

The elements *helium* (He), *neon* (Ne), *argon* (Ar), *krypton* (Kr), *xenon* (Xe) and *radon* (Rn) are grouped together in *Group 18* of the Periodic Table. All of these are gaseous under ordinary conditions of temperature and pressure. The last number of the group *i.e.* radon is obtained from radioactive disintegration of radium. All others are present in air in traces. They are also known as *rare gases* because they are found in very small quantities in nature. They are highly non-reactive and do not take part in chemical combinations to form compounds like other elements and are, therefore, also called *inert gases.*

Because of their inert nature, noble gases always occur in free state. All the noble gases, except radon are present *in air* in small amounts. The relative abundance of noble gases in air is given in Table 10.21. Helium is also present in *natural gas* upto the extent of 10 per cent. It is also present in small quantities in the minerals of radioactive elements. Water from certain *springs* also gives off gases which are rich in helium and argon.

Helium atoms contains two electrons in its outermost shell. All other noble gases possess $\mathbf{ns^2np^6}$ configuration in the outermost electronic shell where *n* represents the principle quantum number. The detailed electronic configurations of noble gases along with their atomic numbers have been given in Table 10.22.

Table 10.22. Electronic Configurations of Noble Gases

Elements	*At. No.*	*Electronic configuration*	*Relative abundance % by volume in air*
Helium (He)	9	$1s^2$	5.2×10^{-4}
Neon (Ne)	10	[He] $2s^2\ 2p^6$	1.8×10^{-3}
Argon (Ar)	18	[Ne] $3s^2\ 3p^6$	9.3×10^{-1}
Krypton (Kr)	36	[Ar] $3d^{10}\ 4s^2\ 4p^6$	1.1×10^{-4}
Xenon (Xe)	54	[Kr] $4d^{10}\ 5s^2\ 5p^6$	8.7×10^{-6}
Radon (Rn)	86	[Xe] $4f^{14}\ 5d^{10}\ 6s^2\ 6p^6$	—

The valence shell electronic configuration for He is $1s^2$ and for other inert gases it is ns^2np^6. In these configuration, the sub-shells belonging to valence shell are fully filled and hence the configurations of inert gases are quite stable. Therefore, atoms of these elements have no tendency to lose or gain electrons and thus do not participate in reactions under normal conditions. *The stable electronic configurations of noble gases are responsible for their inert behaviour.*

Their physical properties show a regular and smooth gradation. Some of the physical constants of the noble gases are listed in Table 10.23.

Table 10.23. Some Properties of Group 18 Elements (Noble Gases)

Element	*Atomic mass*	*Ionisation energy* ($kJ\ mol^{-1}$)	*Density at STP* ($g\ cm^{-3}$)	*Melting point (K)*	*Boiling point (K)*
Helium	4.00	2372	1.8×10^{-4}	—	4.2
Neon	20.18	2080	9.0×10^{-4}	24.6	27.1
Argon	39.10	1520	1.8×10^{-3}	83.8	87.2
Krypton	83.80	1351	3.7×10^{-3}	115.9	119.7
Xenon	131.30	1170	5.9×10^{-3}	161.3	165.0
Radon	222	1037	9.7×10^{-3}	202	211

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General Trends in Physical Properties

1. State. All of them are mono atomic, colourless, odourless and tasteless gases.

2. Solubility. They are sparingly soluble in water. The solubility generally increases with increase in atomic number.

3. Boiling Point and Melting Point. Due to weak intermolecular van der Waal's forces between them they possess very low b. pt. and m. pt. in comparison to those of other substances of comparable atomic and molecular masses. However, the b. pt. and m. pt. increase with increase in atomic number because van der Waal's forces become stronger with increase in size of the atoms or molecules. Therefore, among noble gases radon has the highest m. pt. and b. pt. whereas He has the least m. pt. and b. pt.

4. Liquefication. It is extremely difficult to liquify these gases as there are only weak van der Waal's forces which hold atoms together. Since these forces increase with the increase in atomic size and population of electrons, *ease of liquefication increases down the zero group from He to Rn.*

5. Atomic Radii. In the case of noble gases, the atomic radii correspond to van der Waal's radii. Therefore, these are quite large as compared with atomic radii of the other atoms belonging to the same period. As we go down the group, the van der Waal's radius increases due to the addition of new electronic shells and increase in screening effect.

6. Ionisation Energies. The ionisation energies of noble gases are very high. This is due to the stable configurations of noble gases. However, the ionisation energies decrease with increase in atomic number from He to Rn due to increase in atomic size and decrease in effective nuclear charge.

7. Electron Affinities. Due to the stable np^2np^6 electronic configurations, noble gas atoms have no tendency to accept additional electron. Therefore, their electron affinities are almost zero.

8. Enthalpy of fusion and enthalpy of vapourization. In general, the enthalpies of fusion and the enthalpies of vapourization are low and increase down the group.

Chemical Properties

The noble gases are generally inert and do not participate in the reactions easily. The inertness of noble gases is due to the following reasons :

(*i*) The atoms of noble gases have *stable closed shell electronic configurations.*

(*ii*) The noble gases have *exceptionally high ionization energies.*

(*iii*) The noble gases have *very low electron affinities.*

Prior to 1962, it was thought that nobel gases do not combine at all with other elements and hence no serious attempts were made to synthesize their compounds. However, in 1962, it was observed by N. Bartlett that O_2 reacts with PtF_6 to form the compound $[O_2^+][PtF_6]^-$. In this compound, O_2 is oxidized to O_2^+ by PtF_6. Moreover, since ionization energies of O_2 and xenon are comparable he thought that an analogous reaction should be possible with xenon. He tried the reaction between Xe and PtF_6 by direct interaction and synthesized the first compound of noble gases $Xe^+[PtF_6]^-$ in the form of red crystalline solid.

$$Xe + PtF_6 \longrightarrow Xe^+[PtF_6[^-.$$

Once the reactivity of noble gases was established many more attempts were made to synthesize their compounds. Now many compounds of xenon and krypton are known with fluorine or oxygen. The compounds of krypton are fewer, only the difluoride, KrF_2, has been studied in detail. The compounds of radon have not been isolated so far but have been identified by radiotracer techniques. Lastly, the compounds of He, Ne or Ar are not known.

Compounds of Xenon : Fluorides, Oxides and Oxyfluorides

Xenon forms three fluorides *i.e.*, XeF_2, XeF_4 and XeF_6. These can be obtained by the direct interaction between xenon and fluorine under appropriate experimental conditions.

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$$\underset{(2:1)}{Xe + F_2} \xrightarrow[673\ K]{\text{Nickel tube}} XeF_2$$

$$\underset{(1:5)}{Xe + 2F_2} \xrightarrow[5\text{–}6\ atm]{\text{Nickel tube, 673 K}} XeF_4$$

$$\underset{(1:20)}{Xe + 3F_2} \xrightarrow[50\text{–}60\ atm]{\text{Nickel tube, 575 K}} XeF_6$$

The oxide and oxyfluorides of xenon are obtained from the fluorides. Xenon trioxide can be obtained by the hydrolysis of XeF_4 or XeF_6.

$$2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + 6HF + F_2$$

$$XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$$

The oxyfluorides of xenon namely xenon oxydifluoride ($XeOF_2$) and xenon oxytetrafluoride ($XeOF_4$) are also obtained by the partial hydrolysis of XeF_4 and XeF_6 respectively.

$$XeF_4 + H_2O \longrightarrow XeOF_2 + 2HF$$

$$XeF_6 + H_2O \longrightarrow XeOF_4 + 2HF$$

The fluorides of xenon *i.e.*, XeF_2, XeF_4 and XeF_6 react with fluoride ion acceptors like PF_5, SbF_5, AsF_5 to form adducts in which the fluorides (XeF_2, XeF_4 and XeF_6) change to cationic species whereas the fluoride ion acceptors form flouroanions.

$$XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$$

$$XeF_4 + SbF_5 \longrightarrow [XeF_3]^+ [SbF_6]^-$$

$$XeF_6 + AsF_5 \longrightarrow [XeF_5]^+ [AsF_6]^-$$

Structure of Xenon Compounds

The structure of xenon compounds can be explained on the basis of the VSEPR theory as well as the concept of hybridisation. In the formation of the fluorides of xenon, depending upon the number of Xe-F covalent bonds to be formed *e.g.*, two in XeF_2, four in XeF_4 and six in XeF_6, the electrons in the valence shell of xenon get unpaired. These are promoted to vacant *5d* orbitals. Then depending upon the total pairs of electrons (bond pairs as well as lone pairs) the molecule assumes a particular geometry. This is illustrated in the table given below.

Molecule	*Total elecrtron pairs (BP + LP)*	*Hybridisation*	*Shape*
XeF_2	5	sp^3d	Linear
XeF_4	6	sp^3d^2	Square planar
XeF_6	7	sp^3d^3	Distorted octahedral*

*On the basis of hybridisation, the molecule should have pentagonal bipyramidal structure. However, this structure has not yet been confirmed. Thus, it is preferably believed to have distorted octahedral structure.

The structures of oxyfluorides and oxides of xenon can best be explained by the concept of hybridisation. The types of hybridisation in these molecules and their shapes are listed as follows :

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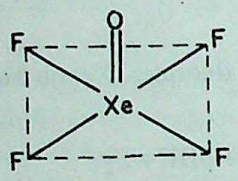
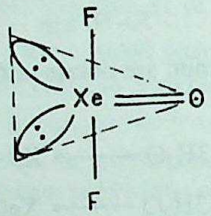
Molecule	*Hybridisation*	*Geometry*	*Shape*
$XeOF_2$	sp^3d	Trigonal bipyramidal	T-shaped
$XeOF_4$	sp^3d^2	Square pyramidal	—
XeO_3	sp^3	Tetrahedral	Pyramidal

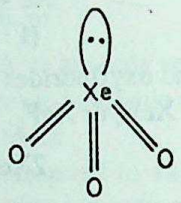
The structures of these compounds are shown below :



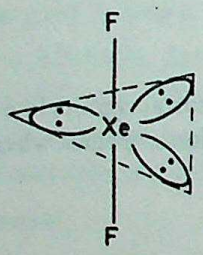
$XeOF_4$
SQUARE PYRAMIDAL



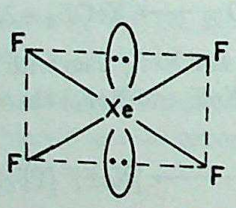
$XeOF_2$
T-SHAPED



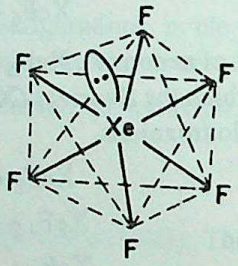
XeO_3
TRIGONAL PYRAMIDAL



XeF_2
LINEAR



XeF_4
SQUARE PLANAR



XeF_6
DISTORTED OCTAHEDRAL

REVIEW QUESTIONS

10.57. Name the most abundant noble gas present in the atmosphere.

10.58. What is the major source of helium ?

10.59. Which noble gas is radioactive ?

10.60. Which element in the Periodic Table has the highest ionisation energy ?

10.61. Which noble gas has the least boiling point ?

10.62. Explain why noble gases have low heats of vapourisation.

10.63. Give formula of the first compound of noble gases.

10.64. Who synthesized the first compound of noble gases ?

10.65. Give shapes of the following molecules :

(*i*) XeF_2 (*ii*) $XeOF_4$ (*iii*) XeF_4.

10.66. What is the state of hybridisation of xenon in the following molecules ?

(*i*) XeF_2 (*ii*) XeO_3 (*iii*) $XeOF_2$.

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10.9. HYDROGEN

Paracelsus, was the first to recognise the formation of hydrogen in sixteenth century from the reaction between iron and sulphuric acid. Later on, in 1766, an English scientist, Henry Cavandish, was able to produce it in pure state by the action of acids on certain metals. He also established it to be a distinct substance and called it *inflammable air* because of its combustible nature. Its name **hydrogen** was proposed by *Lavoisier* because it produces water when burnt in oxygen. *Hydrogen* means *water producer*.

Position of Hydrogen in the Periodic Table

Hydrogen is the first element of the periodic table having atomic number *one*. It has one electron is its K shell and has electronic configuration as $1s^1$. It is difficult to give a proper place to hydrogen in the periodic table because of its resemblance* with halogens as well as alkali metals.

The dual behaviour of hydrogen is attributed to its electronic configuration, *i.e.*, presence of single electron in its K shell. The hydrogen atom has equal tendency to either gain or lose electron in order to acquire stable configuration. When hydrogen atom loses electron it resembles with alkali metals (Group 1). On the other hand, when it gains electron it resembles with halogens (Group 17). Thus, position of hydrogen in the periodic table is anomalous. Some people have gone to the extent of calling hydrogen a *rogue element* because it has not been possible to allot a proper position to hydrogen in the periodic table till today.

The ionisation energy of hydrogen (1312 kJ mol^{-1}) is very high in comparison with the ionisation energies of other metals, *e.g.*, Li = 520 kJ mol^{-1} ; Na = 495 kJ mol^{-1} ; K = 418 kJ mol^{-1}. It is found to be even higher than the first ionisation energy of xenon (1170 kJ mol^{-1}). Thus, it implies that hydrogen has less tendency to lose electrons. Hence, it is found to form essentially covalent bonds in its compounds. Some of the examples of covalent hydrides are HCl, H_2O, NH_3, CH_4, B_2H_6 and a number of organic compounds.

Hydrogen after losing the lone electron from its valence shell leaves a bare proton (H^+ ion). As the size of proton (H^+ ion) is too small ($\sim 1.5 \times 10^{-3}$ pm) it does not exist independently in aqueous solution but it exists in the form of hydrated proton with a formula $H_9O_4^+$. However, for the sake of simplicity hydrated proton is represented by hydronium ion, H_3O^+.

The hydrogen compounds can give H^+ ions only in such solvents which can solvate the protons.

$$HCl + H_2O \longrightarrow [H_3O]^+ + Cl^-$$

Such hydrogen compounds that form solvated hydrogen ions in solvents are called **protonic acids.**

The tendency of hydrogen to gain one electron to form H^- ions is very less. Since the formation of hydride ion (H^-) is an energy consuming process and requires energy of -72.8 kJ mol^{-1}, therefore, the ion can be formed only with those elements which have low ionisation energies, *i.e.*, elements of group 1 and 2.

SOME IMPORTANT TERMS AND PERIODIC TRENDS

- **Diagonal Relationship.** It refers to the similarly in the properties of some of the elements of 2nd period to diagonally opposite elements of 3rd period. The pair of elements showing diagonal resemblance are :

  Li.....Mg ; Be.....Al and B.....Si
- **Charge density.** It is the ratio of charge on the ion to its size.
- **Inert Pair Effect.** It is the reluctance of *s*-electrons of the valence shell to participate in bonding. This effect become more pronounced towards the bottom of each group of the *p*-block elements.
- **Lattice Energy.** It is energy required to break one mole of the solid salt into its ions.

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*Some of the significant points of resemblance and differences of hydrogen with alkali metals and halogens have already been discussed in the previous class.

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- **Hydration Energy.** It is the amount of energy released when one mole of the ions undergo complete hydration in aqueous solution.
- **Covalent Character in Ionic Bond.** In ionic bond the positive ion pulls the electron density of the anion towards itself and brings about polarisation of the anion. This causes the development of some covalent character in ionic bond.
- **Fajan's Rules.** (*i*) Higher the charge density of cation greater is its polarizing power.
  (*ii*) Larger the size of anion greater will be its polarizability.
- **Representative elements.** The elements of *s* and *p*-block of the periodic table are collectively called representative elements.

Group-1 Elements ; Alkali Metals

	INCREASING TRENDS	*DECREASING TRENDS*	*EXCEPTIONS*
Li Na K Rb Cs *Fr ns^1	• Atomic Radii (M) • Ionic Radii M^+ (*g*) • Density • Electropositive character • Chemical reactivity • E° values • Basic strength of metal hydroxides (MOH) • Tendency to form peroxides and super oxides • Reducing nature of metal hydroxides (MH)	• Ionisation Energy • Ionic size M^+ (*aq*) • Extent of Hydration of M^+ • $\Delta H_{Hydration}$ of M^+ • Stability of hydrides (MH) • Strength of intermetallic bonds • Melting and boiling points • Wavelength of colour imparted to flame	• Density of K < Na • Li has lowest E° value • Li is strongest reducing agent

Group-2 Elements ; Alkaline Earth Metals

	INCREASING TRENDS	*DECREASING TRENDS*	*EXCEPTIONS*
Be Mg Ca Sr Ba Ra ns^2	• Atomic Radii (M) • Ionic radii (M^{2+}) • Density • Reducing nature (E° values) • Reactivity • Tendency to form peroxides • Basic strength of hydroxides • Solubility of hydroxides in water • Ionic nature of halides	• IE_1 and IE_2 values • Electronegativity • Tendency to form complexes • diminishes after Mg • Solubility of CO_3^{2-} and SO_4^{2-}	• Density of Ca < Mg • Halides of Be are covalent • BeO and Be $(OH)_2$ are amphoteric

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Group-13 Elements

	INCREASING TRENDS	DECREASING TRENDS	EXCEPTIONS
B Al Ga In Tl $ns^2 np^1$	• Atomic Radii (M) • Ionic Radii • Inert pair effect • Tendency to show + 1 oxidation state • Tendency to form ionic compounds • Electropositive character • Lewis acid strength of trihalides of B increases from $BF_3 \longrightarrow BBr_3$	• Ionisation energies • M.P./B.P. • Tendency to show + 3 oxidation state • Tendency to form covalent compounds	• Atomic size of Ga < In • IE_1 of Tl > In • IE_1 of Ga ≈ Al
	• Behaviour of $M(OH)_3$ change from **acidic** ⟶ **amphoteric** ⟶ **basic** • Compounds of Boron and hydrogen are BORANES which contain three centre 2 electron bond • Compounds of aluminium are ionic as well as covalent		

Group-14 Elements

	INCREASING TRENDS	DECREASING TRENDS	EXCEPTIONS
C Si Ge Sn Pb $ns^2 np^2$	• Atomic Radii • Inert pair effect • Metallic character • Tendency of + 2 oxidation • Tendency of formic ionic compounds • Reducing character of hydrides (MH_4)	• Ionisation energy • Electronegativity • Non-metallic character • Tendency of + 4 oxidation state • Tendency of forming covalent compounds • Thermal stability of hydrides • M—M bond strength • Tendency of catenation	• IE of Pb > Sn IE of Ge ≈ Si • Only C has ability of $p\pi$-$p\pi$ bonding • Si and others can form $d\pi$- $p\pi$ bonding • All elements except Pb show allotropy
	• They form oxides of formula MO and MO_2 • Behaviour of MO_2 change from acidic ⟶ amphoteric ⟶ weakly basic		

Group-15 Elements

	INCREASING TRENDS	DECREASING TRENDS	EXCEPTIONS
N P As Sb Bi $ns^2 np^3$	• Atomic size • Melting/Boiling points increase from N ⟶ As • Metal character • Density • Tendency of lower oxidation state + 3 • Reducing character of hydrides (MH_3) • Ionic character of comp. dominate towards end	• Ionisation energies • Electronegativity • M.P./B.P. decrease As ⟶ Bi • Tendency of covalent bonding • Thermal stability of hydrides • Angle around M in metal hydrides (MH_3) • Basic nature of MH_3 • Acidic character of oxides • Tendency of forming MX_5	• N, P show oxidation state – 3 to + 5 Bi show oxidation state of + 3 only • Elements except N, Bi exhibit allotropy • B.P. of MH_3 $PH_3 < AsH_3 < NH_3 < SbH_3$ • $< BiH_3$
	• Behaviour of oxides change from acidic ⟶ amphoteric ⟶ basic • Their hydrides MH_3 and trihalides are pyramidal put pentahalides are trigonal bipyramidal		

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Group-16 Elements ; Chalcogens

	INCREASING TRENDS	DECREASING TRENDS	EXCEPTIONS
O S Se Te *Po	• Atomic size • Density • Ionic radius • M.P./B.P. increase, O ⟶ Te • Metallic character • Acidic nature of hydrides (H_2X)	• Ionisation energies • Electronegativity • M.P./B.P. decrease, Te ⟶ Po • Electron affinity • Thermal stability of H_2X • Bond angle around X • X—X bond strength	• O shows tendency of $p\pi$-$p\pi$ bonding others can form $d\pi$-$p\pi$ bonding • EA_1 of O < EA_1 of S • S shows some tendency of catenation • X—X bond strength is higest
ns^2 np^4	• B.P. of H_2X : $H_2O > H_2Se > H_2Te > H_2S$ • Atomicity of O is 2 in O_2, 3 in O_3, but those of S, Se, Te is 8 • O shows O.N. of – 2, – 1, + 1, + 2 ; S shows – 2, + 2, + 4, + 6 ; others show + 2, + 4		

Group-17 Elements ; Halogens

	INCREASING TRENDS	DECREASING TRENDS	EXCEPTIONS
F Cl Br I *At	• Atomic size • Ionic radii X^- • Melting/Boiling points • Intensity of colour • Electropositive character • Acidic nature of hydrides (HX) • Reducing nature of hydrides (HX)	• Ionisation energy • Electronegativity • Electron affinity • Chemical reactivity • E° values • Oxidising power • Thermal stability of HX • $\Delta H_{diss.}$ of H—X • Acid strength of HOX	• EA_1 of Cl > EA_1 of F
ns^2 np^5	• Molecular state X_2 • Dissociation energy $[X_2(g) \longrightarrow 2X(g)]$ $I_2 < F_2 < Br_2 < Cl_2$ • F shows oxidation state of – 1 ; others show oxidation state – 1, + 1, + 3, + 5, + 7 • Strength of oxoacids increase with increase in oxidation number of X.		

Group-18 Elements ; Noble Gases

	INCREASING TRENDS	DECREASING TRENDS	EXCEPTIONS
He Ne Ar Kr Xe *Rn	• Atomic size • Polarisability • Magnitude of van der Waal forces M.P./B.P. • Ease of liquefaction • Solubility in water • Reactivity	• Ionisation energy	
ns^2 np^6	• Molecular state is monoatomic • Xe shows oxidation state of + 2, + 4, + 6		

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EXERCISE

VERY SHORT ANSWER QUESTIONS
(1 Marks)

1. Why group 1 elements are known as alkali metals ?
2. Which alkaline earth metal is radioactive ?
3. Why alkali metals are soft ?
4. Why alkali metals are stored under kerosene ?
5. Why alkali metals give blue solutions in liquid ammonia ?
6. Why anhydrous calcium chloride is used as dehydrating agent ?
7. How will you show that $Al(OH)_3$ is amphoteric ?
8. How is lithium aluminium hydride prepared ?
9. What is corrundum ? What is its use ?
10. Why boron has very high melting point ?
11. Which elements exhibits maximum catenation ?
12. What is allotropy ? Name allotropic forms of carbon.
13. What is the oxidation state of nitrogen in HNO_2 ?
14. How is nitric oxide (NO) prepared ?
15. Among hydrides of group 16 elements which has lowest b.p. ?
16. What is the highest oxidation state exhibited by group 16 elements ? Give one compound in this oxidation state.
17. Which halogen has highest electronegativity and which has highest electron affinity ?
18. How do boiling points very among halogens on going down the group ?
19. What is the shape of XeF_4 molecule ?
20. Mention two points illustrating the electropositive character of iodine. *(CBSE 1992)*
21. What is inert pair effect ?
22. What is the common oxidation state of elements of group 13 ?
23. What is the nature of compounds of Lithium ?
24. Which hydride of elements of group 16 has maximum reducing nature ?
25. Which hydride of chalcogen family has highest boiling point and weakest acidic character ?
26. Name the oxide of sulphur which can act as oxidising agent but not reducing agent ?
27. The formation of $F^-(g)$ from $F(g)$ is exothermic but that of $O^{2-}(g)$ from $O(g)$ is endothermic, why ?
28. PH_3 is weaker base than NH_3 although electronegativity of N is greater than that of P, why ?
29. Write the formulae of various oxy acids of chlorine and arrange them in order of increasing acid strength.
30. What is the name of recently developed allotrope of carbon, *i.e.*, C_{60} molecule ? *(I.I.T. 1994)*
31. Anhydrous $AlCl_3$ is covalent but hydrated aluminium chloride is ionic, why ?
32. What is the hybrid state of S in SO_2 and SO_4^{2-} ?
33. Name the alkali metal which is radioactive.
34. What is the hybrid state of Xe in XeF_2, $XeOF_4$ and XeO_3 ?

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35. Which noble gas has highest boiling point but is non-radioactive ?
36. Give example of oxide of chlorine in which oxidation state of Cl is + 6.
37. Give one example each of pseudo halide and pseudohalogen.
38. NO is paramagnetic in gaseous state but diamagnetic in liquid and solid state, why ?
39. What is the reaction of SiF_4 and F^- ions ?
40. The name **drikold** is associated with which chemical species ?

DESCRIPTIVE QUESTIONS

Group 1 Elements

41. Give the general configuration of alkali metals.
42. How do you account for the fact the alkali metals impart characteristic colour to the flame ?
43. Compare the alkali metals and alkaline earth metals with regard to
    (*a*) Volatility, (*b*) Ionization energy,
    (*c*) Basicity of the oxides, and (*d*) Solubility of hydroxides.
44. What is "diagonal relationship" ?
45. Why alkali metals exhibit an oxidation state of + 1 whereas alkaline earth metals an oxidation state of + 2 ?
46. Alkali metals dissolve in liquid ammonia to give deep blue solutions, why ?
47. Complete the following
    (*i*) $Li + CH \equiv CH \longrightarrow$ (*ii*) $Na + O_2 \longrightarrow$
    (*iii*) $K + O_2 \longrightarrow$ (*iv*) $LiOH \xrightarrow{Heat}$
48. Among the alkali metals name the element which has
    (*i*) Strongest reducing character (*ii*) Lowest size of $M^+(g)$ ion
    (*iii*) Highest melting point (*iv*) Lowest IE_1.
49. Why Cs can be used in photoelectric cell but Li cannot be. ***(Pb. Board 1991)***
50. Describe the reaction of alkali metals with O_2. How does the behaviour of their hydroxides vary ?
51. Illustrate the diagonal relationship between lithium and magnesium. ***(Pb. P.M.T. 1992)***

Group 2 Elements

52. How is beryllium chloride prepared ? In what whys does it differ from the halides of other group 2 elements ?
53. Discuss the gradation of (*i*) metallic character and (*ii*) Basic nature of hydroxides among the alkaline earth metals ?
54. Explain why elements of group 2 form M^{2+} ions and not M^{3+} ions.
55. Explain giving reasons :
    (*a*) Alkaline earth metals are poor reducing agents than alkali metals.
    (*b*) The second ionisation energy of alkaline earth metals is greater than the first ionisation energy.
56. Which out of NaOH and $Mg(OH)_2$ is a stronger base and why ?
57. (*a*) Outline a method for the preparation of beryllium chloride and also give its structure.
    (*b*) Explain the solubility of carbonates and hydroxides of the alkaline earth metals down the group. ***(Pb. P.M.T. 1991)***
58. Arrange the (*i*) hydroxides and (*ii*) sulphates of alkaline earth metals in order of decreasing solubilities, giving a suitable reason for each.
59. Explain the following phenomenon by means of balanced equations :
    (*i*) When exhaling in air is made through a tube passing into a solution of line water, solution becomes turbid.

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(*ii*) The turbidity of the solution in (*i*) eventually disappears when continued exhaling is made through it.

(*iii*) When the solution in (*ii*) is heated, turbidity reappears.

60. In what respect does beryllium resemble aluminium ?

61. Arrange the following in order of the property mentioned

(*i*) $BaCl_2$, $MgCl_2$, $BeCl_2$, $CaCl_2$ *increasing ionic character*

(*ii*) $Mg(OH)_2$, $Sr(OH)_2$, $Ba(OH)_2$, $Ca(OH)_2$ increasing solubility in water

(*iii*) BeO, MgO, BaO, CaO increasing basic strength

(*iv*) $Mg(OH)_2$, $Ba(OH)_2$, $Ca(OH)_2$ increasing basic strength. ***(C.B.S.E 1994)***

62. (*a*) What is hydrolith ? How does it react with water ?

(*b*) Out of Ca^{2+}, Ba^{2+}, Mg^{2+} which one has maximum ionic mobility in water ?

Group 13 Elements

63. Write any five points to show diagonal relationship between boron and silicon. ***(Pb. S.B. 1993)***

64. Highlight the difference in the structure of boron trichloride and anhydrous aluminium trichloride.

65. Illustrate ''inert-pair effect'' with reference to the chemistry of group 13 elements.

66. Write balanced equations for the following reactions :

(*i*) $BF_3 + LiH \longrightarrow$ (*ii*) $NaH + B_2H_6 \longrightarrow$

(*iii*) $BF_3 + Me_3N \longrightarrow$ (*iv*) $BCl_3 + H_2O \longrightarrow$

67. Discuss the structure of diborane.

68. Discuss the nature of oxides and hydroxides of boron and aluminium.

69. Why boron does not form B^{3+} ions ?

70. Why the ionisation energy of aluminium is lower than that of magnesium ?

71. Why BF_3 acts as a Lewis acid ?

72. Explain giving equations the amphoteric nature of aluminium oxide.

73. Explain why $Al(OH)_3$ is amphoteric in nature whereas $B(OH)_3$ is acidic ?

74. Discuss the similarities and dissimilarities between boron and aluminium.

75. How does Lewis acid strength varies among trihalides of boron ?

76. Describe the structure of diborane on the basis of hybridisation ?

77. Give the formula of each of the following :

(*i*) Boric acid (*ii*) Sodium metaluminate (*iii*) Inorganic benzene.

Group 14 Elements

78. Compare the structure and properties of CO_2 and SiO_2.

79. Account for the following observations :

(*a*) In trimethylamine, the nitrogen has a pyramidal geometry whereas in trisilylamine $N(SiH_3)_3$ it has a planar geometry. ***(C.B.S.E. 1994)***

(*b*) Elemental silicon does not form a graphite-like structure as carbon does. ***(Delhi P.M.T. 1991)***

80. What are silicones ? How are they manufactured ?

81. Why carbon exhibits catenation to such a large extent whereas other elements of group 14 do not show this property to the same extent ?

82. Explain, why

(*a*) CO_2 is a gas while SiO_2 is a solid ? ***(H.P. Board 1993)***

(*b*) $SnCl_2$ is a solid whereas $SnCl_4$ is a liquid ?

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83. Discuss the structure of silica and explain why it has a high melting point ?

84. Carbon and silicon are always tetravalent but germanium, tin and lead show divalency. Why ?

85. Give reasons for the following :

(*a*) CCl_4 is not hydrolysed with water whereas $SiCl_4$ is hydrolysed.

(*b*) Solid CO_2 is also called dry ice.

86. How does carbon differ from the elements belonging to group 14 of the periodic table ?

87. What are silicates and silicones ? Give one example in each case.

88. Why are Pb (IV) salts are less in adundance ?

89. Among group 14 elements, name the element

(*i*) Which is most electronegative (*ii*) Which has lowest IE_1 value

(*iii*) Which shows maximum tendency of catenation

(*iv*) Which has maximum tendency to form ionic compounds.

90. How do CO_2 and SiO_2 react with carbon ?

Group 15 Elements

91. What is the general configuration and common oxidation states of group 15 elements ?

92. List the various oxidation states of nitrogen and give an example of a compound or ion for each case.

93. Write balanced equations for the following reactions :

(*i*) $PCl_3 + H_2O \longrightarrow$ (*ii*) $SbCl_3 + H_2O \longrightarrow$

(*iii*) $As + Cl_2 \longrightarrow$ (*iv*) $H_3AsO_3(aq) + Zn(s) + H^+(aq) \longrightarrow$

94. Explain giving suitable reasons :

(*a*) NH_3 has a higher boiling point than PH_3.

(*b*) Nitrogen does not form pentahalide but forms pentoxide.

96. Give reasons for the following :

(*a*) Nitrogen forms NF_3 but NF_5 is unknown.

(*b*) Ammonia is distinctly basic while bismuthine is feebly basic.

(*c*) SbF_5 is known but BiF_5 is unknown.

97. Explain why nitrogen is a gas and phosphorous is a solid at room temperature.

98. Explain :

While ammonia is distinctly basic but phosphine is weakly basic, the other hydrides of the group show no basic character at all.

99. Account for the following observations :

(*a*) Molecular nitrogen N_2 is not particularly reactive. *(Pb. S.B. 1992 Supp. ; H.P. Board 1993 ; CBSE 1994)*

(*b*) H_3PO_3 is diprotic. *(IIT Entrance 1989)*

(*c*) Nitrogen forms no pentahalides unlike phosphorus.

100. Give the general formula ano shape of hydrides of elements of 15. Arrange them :

(*i*) in order of decreasing basic strength

(*ii*) in order of increasing bond angle around central atom

(*iii*) in order of decreasing reducing character.

Group 16 Elements

101. Give the names of the elements of group 16. Why are they called *Chalcogens* ?

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102. Account for the following :

(*a*) Water has a higher boiling point than H_2S.

(*b*) SO_2 can act as oxidising as well as reducing agent but SO_3 can act as oxidising agent only.

103. Compare the structure of :

(*a*) SO_2 and SeO_2 (*b*) SO_3 and SeO_3.

104. How do you explain the lack of positive oxidation numbers for oxygen is there any compound in which it exhibit positive oxidation state ?

105. Account for the + 4 and + 6 oxidation states of sulphur. Why can't oxygen show these oxidation states ?

106. Amongst the hydrides of elements of oxygen family, water shows anomalous properties. Why ?

107. Explain why ?

(*a*) Oxygen is a gas while sulphur is a solid at room temperature.

(*b*) Water has high boiling point than hydrogen sulphite.

108. Why tendency to show – 2 oxidation state diminishes from sulphur to polonium ?

(C.B.S.E. 1992 ; Har. Board 1995)

Group 17 Elements

109. Describe the following about halogen family (group 17 elements) :

(*i*) Relative oxidizing power (*ii*) Relative acidic strength of their hydrides

(*iii*) Oxyacids and their relative oxidising ability. ***[A.I. CBSE (O) 1991]***

110. Discuss the trend of the following properties among halogen acids :

(*a*) acidic character (*b*) reducing character.

111. Among fluorine, chlorine, bromine and iodine, which :

(*i*) provides the weakest acid on combination with hydrogen ?

(*ii*) has the smallest ionisation energy ?

(*iii*) forms strongest hydrogen bonds ?

112. Give examples of oxides and oxyacids of halogens in which the oxidation states of halogens are + 1, + 4, + 6 and + 7.

113. How do you explain the higher oxidation states shown by chlorine, bromine and iodine ?

114. Arrange the following in the decreasing order of property indicated :

(*a*) F_2, Cl_2, Br, I_2 — (*Bond energy*)

(*b*) HF, HCl, HBr, HI — (*acid strength (in water)*)

(*c*) M—F, M—Cl, M—Br, M—I — (*Ionic character of the bond*)

(*d*) ClO_4^-, BrO_4^-, IO_4^- — (*Oxidizing power*)

115. Give examples of compounds in which the halogens display positive oxidation states. Which halogen does not show positive oxidation state ?

116. Give balanced equations :

(*a*) $I_2 + NaClO_3 \longrightarrow$ (*b*) $IO_3^- + I^- + H^+ \longrightarrow$ (*c*) $Br_2 + NaI \longrightarrow$

(*d*) $I_2 + S_2O_3^{2-} \longrightarrow$ (*e*) $XeF_2 + H_2O \longrightarrow$

117. Give some examples of interhalogen compounds.

Group 18 Elements

118. What are the reasons for the low reactivity of noble gases ?

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119. (*a*) Describe the preparation of XeF_2 and XeF_4.

(*b*) Give reasons which prompted Bartlet to react xenon with fluorine to form first noble gas compound.

120. Under what conditions would you except compound formation with a noble gas ?

121. Complete the following :

(*a*) $XeF_4 + H_2O \longrightarrow$ (*b*) $XeF_6 + H_2O \longrightarrow$

(*c*) $XeF_6 + PF_5 \longrightarrow$ (*d*) $XeF_6 + NaF \longrightarrow$

122. Give the structural formulae of XeO_3, XeF_6 and $XeOF_4$.

123. What is state of existence of noble gases ? How do melting and boiling points vary among them.

MISCELLANEOUS QUESTIONS

124. Give general characteristics of the alkali metals. Discuss the anomalous behaviour of lithium. Mention two similarities shown by lithium towards magnesium. *(CBSE 1992)*

125. (*a*) Discuss briefly the trends in chemical properties of group 17 elements (Halogen family). Give reasons for anomalous behaviour of fluorine. *(A.I. CBSE 1992, 1993)*

(*b*) Give two examples of the compounds in which halogens show positive oxidation state. *(CBSE 1993)*

126. Discuss briefly the properties of group 16 elements (oxygen-family). Define catenation and illustrate with an example. *(CBSE 1992)*

127. Why does beryllium differ from the rest of alkaline earth metals ? Give general characteristics of the halides of the alkaline earth metals. *(CBSE 1992)*

128. Discuss briefly the trends in chemical properties of group 15 elements (nitrogen family). Why does nitrogen show anomalous behaviour as compared to other members of this group ? *(CBSE 1992)*

129. (*a*) Describe the preparation of XeF_2.

(*b*) Noble gases are relatively inert elements. Give reasons.

130. Complete the following :

(*i*) $BCl_3 + H_2O \longrightarrow$ (*ii*) $LiNO_3 \xrightarrow{Heat}$

(*iii*) $Be_2C + H_2O \longrightarrow$ *(Pb. Board 1993)*

131. Arrange the following in order of the property mentioned

(*i*) PH_3, NH_3, SbH_3, AsH_3 ..... (increasing basic strength) *(CBSE 1994)*

(*ii*) KCl, $MgCl_2$, $CaCl_2$, $BeCl_2$ ..... (increasing ionic character) *(CBSE 1994)*

(*iii*) HF, HCl, HI, HBr ..... (increasing acid strength)

(*iv*) $HClO_4$, HClO, $HClO_2$ ..... (increasing oxidising ability). *(CBSE 1994)*

132. How Xenon form compounds with fluorine even though Xe atom has closed shell electronic configuration ? *(Har. Board 1995)*

133. Explain the solubility of sulphates and hydroxides of alkaline earth metals. *(Pb. Board 1995)*

134. Complete and balance the following :

(*i*) $PbO_2 + HNO_3 \longrightarrow$ (*ii*) $NaBH_4 + I_2 \longrightarrow$ (*iii*) $Ca_3P_2 + H_2O \longrightarrow$ *(CBSE 1995)*

135. Complete the following :

(*i*) $NH_3 + NaOCl \longrightarrow$ (*ii*) $Pb(NO_3)_2 \longrightarrow$ (*iii*) $XeF_6 + KF \xrightarrow{673\ K}$ *(CBSE 1995)*

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136. $(SiH_3)_3N$ is a weaker base than $(CH_3)_3N$, why ? *(I.I.T. 1995)*

137. Why Boron does not form B^+ ion. *(Pb. Board 1997)*

138. What is inert pair effect, illustrate it with reference to boron family. *(Pb. Board 1997)*

139. Contrast the structure and properties of CO_2 and SiO_2. *(Pb. Board 1997)*

140. Element A burns in nitrogen to give an ionic compound B. Compound B reacts with water to give C and D. A solution of C becomes milky on bubbling carbon dioxide. Identify A, B, C, D. *(I.I.T. 1997)*

141. Arrange the following sulphates of alkaline earth metals in order of decreasing thermal stability :

$BeSO_4$, $MgSO_4$, $CaSO_4$, $SrSO_4$. *(I.I.T. 1997)*

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select correct answer from each of the following questions :

1. The basic strength of which hydroxide is maximum
   (*a*) LiOH (*b*) $SO_2(OH)_2$ (*c*) $Ca(OH)_2$ (*d*) KOH.
2. The similarity in the properties of alkali metals is due to
   (*a*) their same atomicity (*b*) similar outer shell configuration
   (*c*) same energy of outershell (*d*) same principal quantum number of outer shell.
3. CsOH is
   (*a*) strongly basic (*b*) weakly basic (*c*) slightly acidic (*d*) amphoteric.
4. K^+ ion is isoelectronic with
   (*a*) Na^+ (*b*) Ne (*c*) Ar (*d*) Cs^+.
5. Which of the following decomposes on heating ?
   (*a*) LiOH (*b*) NaOH (*c*) KOH (*d*) CsOH.
6. Among the alkali metals most abundant metal is
   (*a*) Na (*b*) K (*c*) Li (*d*) Cs.
7. The highest melting alkali metal is
   (*a*) Li (*b*) Na (*c*) Cs (*d*) Rb.
8. In the presence of excess oxygen, on heating, lithium forms
   (*a*) LiO (*b*) LiO_2 (*c*) Li_2O (*d*) Li_2O_2.
9. Which of the following metals is most commonly used in photo-chemical cells ?
   (*a*) Lithium (*b*) Calcium (*c*) Caesium (*d*) Francium.
10. Size of Na^+ ion is same as that of
    (*a*) Ne atom (*b*) Na atom (*c*) K atom (*d*) None of these.
11. Which of the following compounds is most soluble is water ?
    (*a*) $MgSO_4$ (*b*) $CaSO_4$ (*c*) $SrSO_4$ (*d*) $BaSO_4$.
12. Of the following, an amphoteric hydroxide is
    (*a*) $Ca(OH)_2$ (*b*) NaOH (*c*) $Be(OH)_2$ (*d*) LiOH.
13. Ca^{2+} is isoelectronic with
    (*a*) Mg^{2+} (*b*) Kr (*c*) Ar (*d*) Na^+.
14. Which of the following decomposes at highest temperature ?
    (*a*) $SrCO_3$ (*b*) $BaCO_3$ (*c*) $CaCO_3$ (*d*) $MgCO_3$.
15. Which of the following electronic configurations in the outermost two shells is characteristic of the alkaline earth metals ?
    (*a*) $(n-1)\,s^2p^6ns^2$ (*b*) $(n-1)\,s^2p^6d^{10}ns^2$
    (*c*) $(n-1)\,s^2p^6ns^2p^1$ (*d*) None of these.

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16. In B_2H_6
(a) there is a direct boron-boron bond (b) the boron atoms are linked through hydrogen bridges
(c) the structure is similar to C_2H_6 (d) all the atoms are in one plane.

17. B_2O_3 is
(a) Acidic (b) Basic (c) Amphoteric (d) None of these.

18. Which of the following hydrides is most stable ?
(a) CH_4 (b) SiH_4 (c) PbH_4 (d) SnH_4.

19. Which of the following is most abundant in earth's crust
(a) C (b) Si (c) Ge (d) Sn.

20.. Which of the following bonds has highest bond energy ?
(a) C—C (b) Si—Si (c) Ge—Ge (d) Sn—Sn.

21. Which of the following does not exhibit allotropy ?
(a) Carbon (b) Silicon (c) Tin (d) Lead.

22. The most stable hydride of group 15 elements is
(a) NH_3 (b) PH_3 (c) AsH_3 (d) SbH_3.

23. Which of the following compounds is least basic ?
(a) NH_3 (b) PH_3 (c) AsH_3 (d) SbH_3.

24. Which of the following has lowest b.pt. ?
(a) Nitrogen (b) Arsenic (c) Phosphorus (d) Antimony.

25. Which of the following compounds does not exist ?
(a) PCl_5 (b) $AsCl_5$ (c) $SbCl_5$ (d) $BiCl_5$.

26. Which of the following exists as diatomic molecule ?
(a) Nitrogen (b) Arsenic (c) Phosphorus (d) Antimony.

27. The most common oxidation state for oxygen is
(a) + 2 (b) – 2 (c) + 4 (d) + 6.

28. Which one of the following elements does not show an oxidation state higher than + 2 ?
(a) Oxygen (b) Sulphur (c) Selenium (d) Tellurium.

29. Which one of the following hydrides of the elements of group 16 is a liquid ?
(a) H_2O (b) H_2S (c) H_2Se (d) H_2Te.

30. Water is a liquid due to the presence of
(a) ionic bonding (b) covalent bonding (c) odd electron bond (d) hydrogen bonding.

31. Oxygen and sulphur are alike as both
(a) can form covalent compounds with metals (b) exist in diatomic state
(c) have atoms of same size (d) can form covalent hydrides.

32. The high oxidizing power of fluorine is due to
(a) high electron affinity (b) high heat of dissociation and low heat of hydration
(c) high heat of hydration and low heat of dissociation (d) high heat of hydration and high heat of dissociation.

33. The greater reactivity of fluorine is due to
(a) lower energy of F—F bond (b) high energy of F—F bond
(c) F_2 is a gas at room temperature (d) none of these is correct.

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34. Halogens are all coloured
(*a*) due to absorption of U-V light (*b*) due to absorption of I.R. light
(*c*) due to absorption of visible light (*d*) none of the above is correct.

35. The halogens are chemically similar because
(*a*) for each element, the atomicity is 2
(*b*) their outermost electrons have the same principal quantum number
(*c*) their atoms can lose 7 electrons to form ions with the electronic structure of an inert gas
(*d*) they each have atoms which need only one electron to fill completely a outermost *p*-sub-shell.

36. Which of the following has the highest b.pt. ?
(*a*) Xe (*b*) Kr (*c*) Ar (*d*) He.

37. Which of the following has highest first ionization energy ?
(*a*) He (*b*) Ne (*c*) Ar (*d*) Kr.

38. Which noble gas was detected first of all ?
(*a*) Helium (*b*) Neon (*c*) Argon (*d*) Xenon.

39. Which of the noble gases is most reactive ?
(*a*) He (*b*) Ne (*c*) Kr (*d*) Xe.

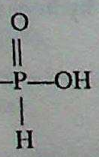
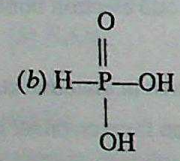
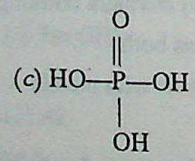
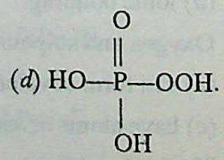
40. Which of the following does not have S—S bond ?
(*a*) $S_2O_4^{2-}$ (*b*) $S_2O_3^{2-}$ (*c*) $S_2O_5^{2-}$ (*d*) $S_2O_7^{2-}$. *(I.I.T. 1991)*

41. Which acid forms two series of salts ?
(*a*) H_3PO_4 (*b*) H_3PO_3 (*c*) H_3BO_3 (*d*) H_3PO_2.
(CEET Kurukshetra 1996)

42. Which of the following hydrogen halide is most volatile
(*a*) HF (*b*) HCl (*c*) HBr (*d*) HI.
(CEET Kurukshetra 1996)

43. The correct order of thermal stability among the following :
K_2CO_3 (I), $MgCO_3$ (II), $CaCO_3$ (III), $BeCO_3$ (IV)
(*a*) I < II < III < IV (*b*) IV < II < III < I (*c*) IV < II < I < III (*d*) II < IV < III < I.

44. Which of the following species in not a pseudohalide ?
(*a*) CNO^- (*b*) $RCOO^-$ (*c*) OCN^- (*d*) SCN^-. *(I.I.T. 1997)*

45. The formula of hypophosphorus acid is
(*a*) 
(*b*) 
(*c*) 
(*d*) 
(CBSE Ent. 1997)

ASSERTION-REASON TYPE QUESTIONS

In each of the following questions two statements are given, one of the statement is labbled as *Assertion A* while the other one as *Reason R*. Examine the two statements carefully and mark the correct choice *a*, *b*, *c* or *d* according to the following instructions

(*a*) If both A and R are correct and R is correct explanation of A

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(*b*) If both A and R are correct but R is not the explanation of A

(*c*) If A is correct but R is wrong

(*d*) If A is wrong but R is correct.

46. *Assertion A* : Among chalogens tendency of catenation is maximum for sulphur.

Reason R : S—S bond is stronger than O—O bond.

(*a*) (*b*) (*c*) (*d*)

47. *Assertion A* : The m.p./b.p. of noble gas are quite high.

Reason R : The interparticle forces among noble gases in their liquid state are van der Waal forces.

(*a*) (*b*) (*c*) (*d*)

48. *Assertion A* : Carbon monoxide reacts with Ni to form $Ni(CO)_4$.

Reason R : Carbon monoxide is amphoteric oxide.

(*a*) (*b*) (*c*) (*d*)

49. *Assertion A* : $B(OH)_3$ is acidic while $In(OH)_3$ is basic.

Reason R : $B(OH)_3$ is a highly H-bonded structure.

(*a*) (*b*) (*c*) (*d*)

50. *Assertion A* : The compound called inorganic benzene is borazine.

Reason R : Borazine has structural similarity with benzene.

(*a*) (*b*) (*c*) (*d*)

51. *Assertion A* : PCl_5 is covalent in gaseous and liquid state but ionic in solid state.

Reason R : The solid state of PCl_5 consists of tetrahedral cation and octahedral anion.

(*a*) (*b*) (*c*) (*d*)

52. *Assertion A* : H_3PO_3 is a dibasic compound.

Reason R : Two H atoms are directly attached to P.

(*a*) (*b*) (*c*) (*d*) **(AIIMS 1997)**

53. *Assertion A* : Li resembles Mg.

Reason R : Li^+ has almost same size as Mg^{2+}.

(*a*) (*b*) (*c*) (*d*) **(AIIMS 1997)**

54. *Assertion A* : Pb^{4+} can be reduced to Pb^{2+} easily.

Reason R : Pb^{2+} is paramagnetic.

(*a*) (*b*) (*c*) (*d*) **(AIIMS 1997)**

FILL IN THE BLANKS

Fill in the blanks with appropriate items :

1. Lithium resembles more ..... than sodium.
2. Sodium is ..... electropositive than potassium.
3. I_2 dissolves in KI(*aq*) to form ..... .
4. As the size of the cation ..... the basicity of the corresponding hydroxide increases.
5. ..... is manufactued by Haber's process.
6. The formula of laughing gas is ..... .

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7. Most common oxidation state of group 5 elements is ..... .
8. The brown ring in the test for nitrate is due to ..... .
9. Bismuth does not exhibit penta valency because of ..... .
10. B_2H_6 is an ..... compound.
11. $N(SiH_3)_3$ has ..... geometry.
12. Be shows diagonal relationship with ..... .
13. CN^- is an example of ..... halide ion.
14. The hybrid state of C in diamond and in graphite is ..... and ..... respectively.
15. ..... is the first compound of noble gas prepared by ..... in 1962.
16. The basicity of H_3PO_4 is ..... . *(I.I.T. 1990)*
17. ..... acid gives ..... ion (Hypobromic, hypobromous, bromide, bromite, perbromate). *(I.I.T 1989)*
18. An oxide of nitrogen which is isostructural and isoelectronic with carbon dioxide is ..... . *(M.L.N.R. 1990)*
19. The hydrolysis of monoalkyltrichloro silane gives ..... . *(I.I.T. 1994)*
20. The tendency of atoms to undergo self-linking to form long chains or ring skeletons called ..... .
21. In the reaction; $I_2 + I^- \longrightarrow I_3^-$, the Lewis acid is ..... . *(I.I.T. 1997)*
22. The compounds that formally contain Pb^{4+} are easily reduced to Pb^{2+}. The relative stability of lower oxidation state is due to ..... . *(I.I.T. 1997)*
23. Among PCl_3, CH_3^+, NH_2^- and NF_3, ... is least reactive towards water. *(I.I.T. 1997)*
24. The angle P—P—P in P_4 molecule is ..... degree ..... . *(I.I.T. 1997)*
25. On heating $RbICl_2$ will decompose to give ..... . *(I.I.T. 1997)*

TRUE/FALSE STATEMENTS

1. Arsenic is a metal.
2. Bismuth is a metalloid.
3. Phosphorus exists as tetra atomic molecules.
4. NCl_5 is covalent in nature.
5. PH_3 is pyramidal in shape.
6. Aqueous solution of ammonia turns blue litmus red.
7. Nitrous acid can act as oxidizing as well as reducing agent.
8. Boron exists as B^{3+} in most of its compounds.
9. Boric acid is a monobasic acid.
10. Phosphorus can form $d\pi - p\pi$ bond with oxygen.
11. Diborane is a co-ordinate compound.
12. Aluminium is the most abundant element of group 3.
13. Sulphur does not show oxidation state of – 2 in any of its compound.
14. $p\pi - p\pi$ bonding is not shown by silicon.
15. Ionisation energy (IE_1) of Sn > than that of Pb.
16. H—F is stronger acid as compared to HI.
17. In SF_4 molecule S-atom assumes sp^3 hybrid state.

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18. BBr_3 is stronger Lewis acid than BF_3.
19. Alkali metals are very good reducing agents.
20. Chalcogens is the name given to elements of group 17.

ANSWERS/HINTS

REVIEW QUESTIONS

10.1. Li
10.3. + 1
10.4. They attain noble gas configuration after losing 1st electron
10.5. Li
10.6. Ionic
10.9. LiOH, CsOH
10.10. (*i*) $Li_2CO_3 \longrightarrow Li_2O + CO_2$ (*ii*) Na_2CO_3 does not decompose
10.11. Ca
10.12. Mg
10.13. + 2
10.14. Be
10.16. $CaO + H_2O \longrightarrow Ca(OH)_2$
10.17. $Ba(OH)_2$ solution
10.18. $BeCO_3$
10.20. $Be(OH)_2$ is amphoteric, $Mg(OH)_2$ is a weak base
10.21. B
10.23. B
10.25. H_3BO_3
10.27. BBr_3
10.29. Carbon
10.30. + 4 and – 2
10.31. Carbon
10.33. Carbon
10.34. CH_4
10.36. Nitrogen
10.37. – 3, – 3, + 5
10.38. $\ddot{N}H_3$
10.40. $:\ddot{O}:N::\ddot{O}:$
10.42. + 3
10.43. PCl_5
10.44. Oxygen
10.45. Sulphur
10.46. oxygen
10.47. H_2Te, H_2O
10.48. (*i*) sp^3d^2, (*ii*) sp^3d (*iii*) sp^2
10.51. Solid
10.52. (*i*) F (*ii*) Cl (*iii*) F
10.53. F
10.54. (*i*) H—F (*ii*) H—I (*iii*) H—Cl
10.55. sp^3d, sp^3d^2
10.56. Ar
10.58. Sun
10.59. He
10.60. He
10.62. $Xe^+ [PtCl_6]^-$
10.63. N. Bartlet
10.65. (*i*) sp^3d (*ii*) sp^3 (*iii*) sp^3d.

VERY SHORT ANSWER QUESTIONS

2. Radium
3. Due to weak metallic bond
4. To prevent their reaction with air and moisture
5. Due to ammoniated electrons
6. Because it absorbs moisture and forms $CaCl_2 . 6H_2O$
7. Because it exists as B_{12} molecule having strong B—B bonds
10. Carbon
13. + 3
15. H_2S
16. + 6, SF_6
17. F, Cl
18. Increase down the group
19. Square planar
20. Lustre and existence of I^+ and I^{3+}.
25. H_2O
26. SO_3
30. Buckminsterfullerene.
31. Formation of Al^{3+} requires high amount of ionisation energy ($IE_1 + IE_2 + IE_3$). Hence Al links with chlorine atoms by covalent bonds. In aqueous solution hydration of aluminium chloride occurs. The high amount of hydration energy helps the ionisation of Al. More over in dissolved state it exists as $[Al(H_2O)_6]^{3+}$ complex ion.

$$AlCl_3 + 6H_2O \longrightarrow [Al(H_2O)_6]^{3+} + 3Cl^- + \text{Energy}$$

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32. sp^2 and sp^3 **33.** Francium **35.** Xe

36. Cl_2O_6 **37.** CN^- and $(CN)_2$

38. NO molecule has eleven electrons. This, it contains odd number of electron. It is therefore, paramagnetic in gaseous state. However, in solid and liquid state, it forms a loose dimer in such a way that magnetic field of unpaired electrons of two molecules cancel out. As a result it becomes diamagnetic.

39. $SiF_4 + 2F^- \longrightarrow [SiF_6]^{2-}$ **40.** Solid carbon dioxide is called dry ice and has drikold as commercial name.

DESCRIPTIVE QUESTIONS

47. (*i*) $2Li + CH \equiv CH \longrightarrow LiC \equiv CLi + H_2$ (*ii*) $2Na + O_2 \longrightarrow Na_2O_2$

(*iii*) $K + O_2 \longrightarrow KO_2$ (*iv*) $LiOH \xrightarrow{Heat} Li_2O + H_2O$

48. (*i*) Li (*ii*) Li (*iii*) Li (*iv*) Cs

61. (*i*) $BeCl_2, MgCl_2, CaCl_2, BaCl_2$ (*ii*) $Mg(OH)_2, Ca(OH)_2, Sr(OH)_2, Ba(OH)_2$

(*iii*) BeO, MgO, CaO, BaO (*iv*) $Mg(OH)_2, Ca(OH)_2, Ba(OH)_2$

62. (*a*) Hydrolith is CaH_2 ; $CaH_2 + 2H_2O \longrightarrow Ca(OH)_2 + H_2$ (*b*) Ba^{2+}

66. (*i*) $2BF_3 + 6LiH \longrightarrow B_2H_6 + 6LiF$ (*ii*) $2NaH + B_2H_6 \longrightarrow 2NaBH_4$

(*iii*) $Me_3N + BF_3 \longrightarrow [Me_3N \rightarrow BF_3]$ (*iv*) $BCl_3 + 3H_2O \longrightarrow H_3BO_3 + 3HCl$

77. (*i*) H_3BO_3 (*ii*) $NaAlO_2$ (*iii*) $B_3N_3H_6$

93. (*i*) $PCl_3 + 3H_2O \longrightarrow H_3PO_3 + 3HCl$ (*ii*) $SbCl_3 + H_2O \longrightarrow SbOCl + 2HCl$

(*iii*) $4As + 6Cl_2 \longrightarrow 4AsCl_3$ (*iv*) $2H_3AsO_3 + 3Zn + 6H^+ \longrightarrow 2As + 3Zn^{2+} = 6H_2O$

116. (*a*) $I_2 + 2NaClO_3 \longrightarrow 2NaIO_3 + Cl_2$ (*b*) $IO_3^- + 5I^- + 6H^+ \longrightarrow 3I_2 + 3H_2O$

(*c*) $Br_2 + 2NaI \longrightarrow 2NaBr + I_2$ (*d*) $I_2 + 2S_2O_3^{2-} \longrightarrow 2I^- + S_4O_6^{2-}$ (tetrathionate)

(*e*) $2XeF_2 + 2H_2O \longrightarrow 2Xe + 4HF + O_2$

121. (*a*) $2XeF_4 + 3H_2O \longrightarrow Xe + XeO_3 + F_2 + 6HF$ (*b*) $XeF_6 + 3H_2O \longrightarrow XeO_3 + 6HF$

(*c*) $XeF_6 + PF_5 \longrightarrow [XeF_4]^+[PF_6]^-$ (*d*) $XeF_6 + 2NaF \longrightarrow Na_2XeF_8$

130. (*ii*) $LiNO_3 \longrightarrow 2Li_2O + 4NO_2 + O_2$ (*iii*) $Be_2C + H_2O \longrightarrow 2BeO + CH_4$

131. (*i*) AsH_3, SbH_3, PH_3, NH_3 (*ii*) $BeCl_2, MgCl_2, CaCl_2, KCl$

(*iii*) HF, HCl, HBr, HI (*iv*) $HClO, HClO_2, HClO_4$

134. (*i*) $PbO_2 + HNO_3 \longrightarrow Pb(NO_3)_2 + H_2O + \frac{1}{2}O_2$

(*ii*) $NaBH_4 + I_2 \longrightarrow B_2H_6$ (*iii*) $Ca_3P_2 + 6H_2O \longrightarrow 3Ca(OH)_2 + 2PH_3$

135. (*i*) $2NH_3 + NaOCl \longrightarrow N_2H_4 + NaCl + H_2O$

(*ii*) $Pb(NO_3)_2 \longrightarrow PbO + 2NO_2 + \frac{1}{2}O_2$ (*iii*) $XeF_6 + 2KF \longrightarrow K_2XeF_8$

136. Lone pair of N in $(SiH_3)_3N$ is used up in forming $p\pi$-$d\pi$ bond with Si-atom. Hence its basic strength is considerably reduced.

140. A is Ca, B is Ca_3N_2, C is $Ca(OH)_2$, D is NH_3, milkyness is $CaCO_3$.

MULTIPLE CHOICE QUESTIONS

1. (*d*)	**2.** (*b*)	**3.** (*a*)	**4.** (*c*)	**5.** (*a*)	**6.** (*a*)
7. (*a*)	**8.** (*c*)	**9.** (*c*)	**10.** (*d*)	**11.** (*a*)	**12.** (*c*)
13. (*c*)	**14.** (*b*)	**15.** (*a*)	**16.** (*b*)	**17.** (*a*)	**18.** (*a*)
19. (*b*)	**20.** (*a*)	**21.** (*a*)	**22.** (*a*)	**23.** (*d*)	**24.** (*a*)

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25. (*d*)	26. (*a*)	27. (*b*)	28. (*a*)	29. (*a*)	30. (*d*)
31. (*d*)	32. (*c*)	33. (*a*)	34. (*c*)	35. (*d*)	36. (*a*)
37. (*a*)	38. (*a*)	39. (*d*)	40. (*d*)	41. (*b*)	42. (*b*)
43. (*b*)	44. (*b*)	45. (*a*)	46. (*a*)	47. (*d*)	48. (*c*)
49. (*b*)	50. (*a*)	51. (*b*)	52. (*c*)	53. (*a*)	54. (*c*)

FILL IN THE BLANKS

1. Mg	2. less	3. KI_3
4. increases	5. NH_3	6. N_2O
7. + 3	8. $FeSO_4.NO$	9. inert pair effect
10. electron deficient	11. planar	12. Aluminium
13. pseudo	14. sp^3 and sp^2	15. $XePtF_6$
16. 3	17. Hypobromous, bromite	18. N_2O
19. Highly cross linked	20. Catenation	21. I_2
22. Inert pair effect	23. CH_3^+	24. 60°
25. Rb^+ and ICl_2^- ions		

TRUE/FALSE STATEMENTS

1. False	2. False	3. True	4. False	5. True	6. False
7. True	8. False	9. False	10. True	11. False	12. True
13. False	14. True	15. False	16. False	17. False	18. True
19. True	20. True.				

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11

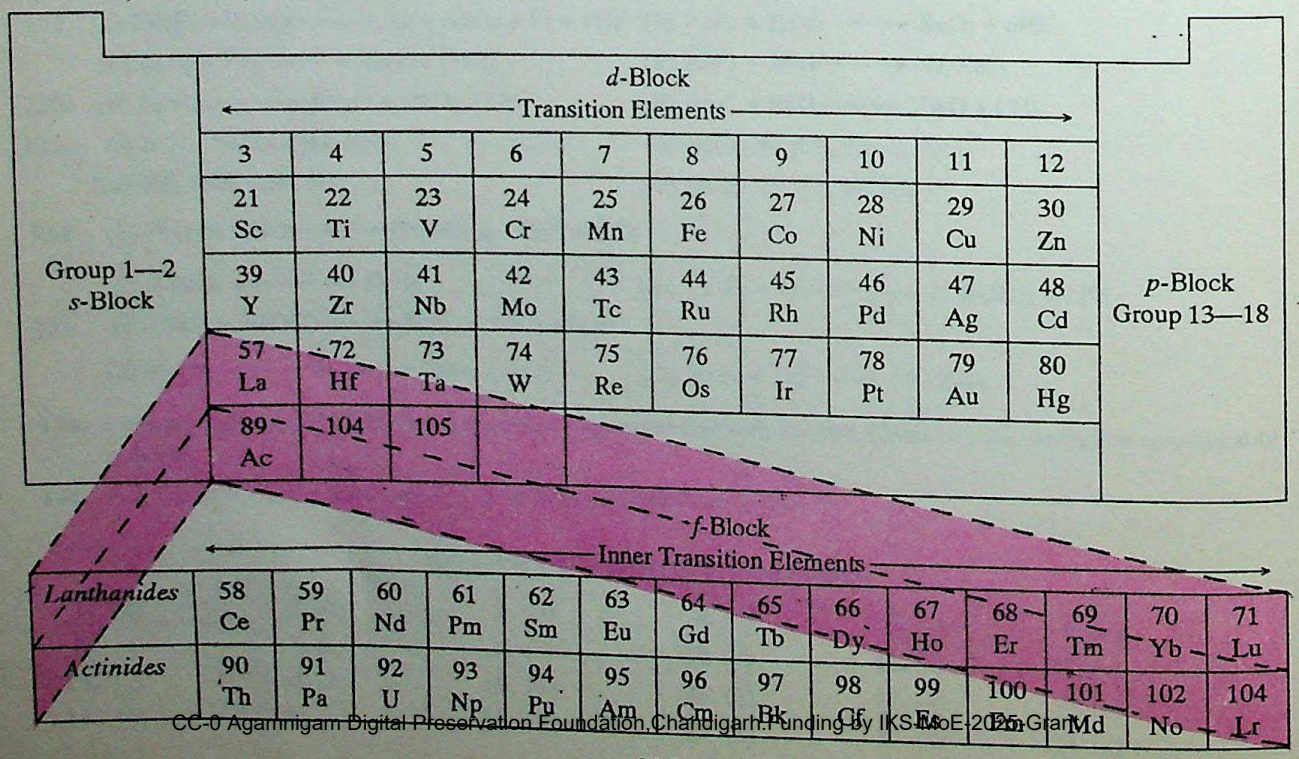
Transition Metals Including Lanthanides

LEARNING OBJECTIVES

In this unit, we shall learn :

- *Electronic configuration, general characteristic properties, oxidation states of transition metals*
- *General properties of second and thrird row of transition elements (Groupwise discussion)*
- *Preparation of potassium dichromate, potassium permanganate*
- *Inner transition elements ; General discussion with special reference to oxidation states and lanthanide contraction*

In periodic table, the elements are classified into four blocks namely ; *s, p, d* and *f* after the name of the atomic orbital which receives the last electron. The *d*-block elements are called transition elements. This block consists of elements lying between *s*- and *p*-blocks starting from fourth period and onwards. These elements possess properties that are transitional between the *s*- and *p*-block elements. In other words, *they represent transition or change in properties from s-block to p-block and are, therefore, called transition elements.* The **transition elements** may be defined ***as the elements whose atoms or simple ions contain partially filled d-orbitals.*** This definition of transition elements does not cover *zinc, cadmium* and *mercury* which are, however, included in the transition elements.



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All the elements belonging to this section are metals. Most of the transition metals have immense industrial importance. For example, the precious metals, gold, platinum, palladium, silver, etc., and commonly used metals such as iron, copper, mercury, etc., all belong to transition elements. In this unit, we shall discuss the general characteristics of transition elements and also that of lanthanides.

11.1. ELECTRONIC CONFIGURATIONS

In the transition elements, *d*-orbitals are successively filled. There are three transition series. The **first transition series** involves the filling of 3*d* orbitals. It starts from *scandium* (Z = 21) and goes up to *zinc* (Z = 30).

The **second transition series** involves the filling of 4*d*-orbitals and includes 10 elements from *yttrium* (Z = 39) to *cadmium* (Z = 48).

The **third transition series** involves filling of 5*d*-orbitals. The first element of this series is *lanthanum* (Z = 57). It is followed by fourteen elements called lanthanides which involve the filling of 4*f*-orbitals. The next nine elements from *hafnium* (Z = 72) to *mercury* (Z = 80) belong to third transition series.

The general electronic configuration of transition elements is $(n-1)\ d^{1-10}\ ns^{1-2}$. The electronic configurations of the three transition series are given in Table 11.1.

Table 11.1. Electronic Configurations of Transition Elements

First Transition Series			*Second Transition Series*			*Third Transition Series*		
Atomic number	*Element*	*Electronic configuration*	*Atomic number*	*Element*	*Electronic configuration*	*Atomic number*	*Element*	*Electronic configuration*
21	Sc	[Ar] $3d^1\ 4s^2$	39	Y	[Kr] $4d^1\ 5s^2$	57	La	[Xe] $5d^1\ 6s^2$
22	Ti	[Ar] $3d^2\ 4s^2$	40	Zr	[Kr] $4d^2 5s^2$	72	Hf	[Xe] $4f^{14}\ 5d^2\ 6s^2$
23	V	[Ar] $3d^3\ 4s^2$	41	Nb	[Kr] $4d^4\ 5s^1$	73	Ta	[Xe] $4f^{14}\ 5d^3\ 6s^2$
24	Cr	[Ar] $3d^5\ 4s^1$	42	Mo	[Kr] $4d^5\ 5s^1$	74	W	[Xe] $4f^{14}\ 5d^4\ 6s^2$
25	Mn	[Ar] $3d^5\ 4s^2$	43	Tc	[Kr] $4d^5\ 5s^2$	75	Re	[Xe] $4f^{14}\ 5d^5\ 6s^2$
26	Fe	[Ar] $3d^6\ 4s^2$	44	Ru	[Kr] $4d^7\ 5s^1$	76	Os	[Xe] $4f^{14}\ 5d^6\ 6s^2$
27	Co	[Ar] $3d^7\ 4s^2$	45	Rh	[Kr] $4d^8\ 5s^1$	77	Ir	[Xe] $4f^{14}\ 5d^7\ 6s^2$
28	Ni	[Ar] $3d^8\ 4s^2$	46	Pd	[Kr] $4d^{10}\ 5s^0$	78	Pt	[Xe] $4f^{14}\ 5d^9\ 6s^1$
29	Cu	[Ar] $3d^{10}\ 4s^1$	47	Ag	[Kr] $4d^{10}\ 5s^1$	79	Au	[Xe] $4f^{14}\ 5d^{10}\ 6s^1$
30	Zn	[Ar] $3d^{10}\ 4s^2$	48	Cd	[Kr] $4d^{10}\ 5s^2$	80	Hg	[Xe] $4f^{14}\ 5d^{10}\ 6s^2$

It would be of interest to consider the change in the relative energies of various sub-shells with change in atomic number. The relative energies of sub-shells of third, fourth and fifth energy levels are given in Fig. 11.1.

As is clear from the Fig. 11.1, upto Z = 20, 4*s* sub-shell has lower energy than 3*d* sub-shell. Therefore, calcium (Z = 20) has the electronic configuration $1s^2\ 2p^2\ 2p^6\ 3s^2\ 3p^6\ 4s^2$. Beyond this there is a sharp decrease in the energy of 3*d* sub-shell and its energy becomes less than the 4*s* sub-shell. Starting with scandium (Z = 21) up to zinc (Z = 30), the 3*d* orbitals are filled and the *d*-electrons become more effective in shielding the 4*s* electrons from the attractive force of the nucleus. Therefore, 3*d* sub-shell gets pulled lower than 4*s*. It may be noted that *when atoms of these elements change into cations, the electrons are removed from 4s-orbital instead of 3d-orbitals although the former was filled earlier.* For example,

$$_{26}Fe : [Ar]\ 3d^6\ 4s^2 \qquad Fe^{2+} : [Ar]\ 3d^6$$

$$_{27}Co : [Ar]\ 3d^7\ 4s^2 \qquad Co^{2+} : [Ar]\ 3d^7$$

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Similar pattern is again repeated in the fifth period where the 5*s*, 4*d* and 6*s*, 5*d*-orbitals are involved in second and third transition series respectively. In lanthanum, however, the energies of 4*f*, 5*d* and 6*s* orbitals are very close to one another and one electron enters the 5*d* orbital before 4*f* begins to fill.

The outer electronic configuration of lanthanum is $5d^1\ 6s^2$. In the subsequent elements, the 4*f* subshell is stabilised relative to the 5*d* subshell. Since there are seven 4*f* orbitals, a total number of 14 elements result before the 5*d* orbitals begin to fill up. The transition elements consist of the elements scandium (Z = 21) to zinc (Z = 30) ; yttrium (Z = 34) to cadmium (Z = 48), lanthanum (Z = 57), hafnium (Z = 72) to mercury (Z = 80) and actinium (Z = 89), which involve the filling of their 3*d*, 4*d*, 5*d* and 6*d* orbitals. The fourteen elements immediately following lanthanum constitute the first inner transition series. These elements are from cerium (Z = 58) to lutetium (Z = 71) in which the 4*f* orbitals are being filled successively. These are called **lanthanides.** The elements of second inner transition series are called **actinides.** They consist of fourteen elements from Actinium (Z = 89) to Lawrencium (Z = 103). In these elements, the 5*f* orbitals are successively filled.

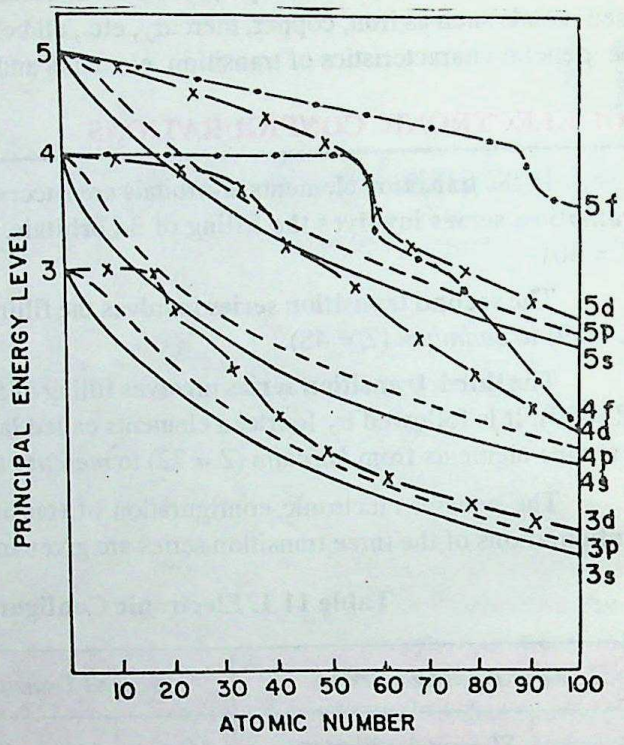

Fig. 11.1. Energies of orbitals of third, fourth and fifth energy levels as a function of atomic number.

11.2. PHYSICOCHEMICAL PROPERTIES

Transition elements having partly filled *d*-orbitals exhibit several interesting properties. For example, they exhibit variable oxidation states, form coloured complexes with different anions and neutral molecules, show paramagnetic behaviour. Transition metals and their compounds also possess catalytic properties. Zinc, cadmium and mercury possess fully filled *d*-orbitals and hence do not exhibit these characteristic properties. Some of the important properties of transition metals are discussed below :

1. Metallic Character

All transition elements are metallic in nature and nearly all of them have simple hcp, ccp or bcc lattices. They show gradual decrease in electropositive character in moving from left to right. The metallic bonds in transition metals are quite strong. This is due to the greater effective nuclear charge and the large number of valence electrons. ***Due to the presence of strong metallic bonds, the transition metals are hard, possess high densities and high enthalpies of atomisation.*** Most of the transition elements have densities higher than 5 g cm^{-3}, the highest being that of osmium (22.6 g cm^{-3}).

2. Melting and Boiling Points

The melting and boiling points of transition elements are generally very high. *This is due to strong metallic bond and the presence of half-filled d-orbitals in them. Due to these half-filled orbitals, some covalent bonds also exist between atoms of transition elements.* ***Because of stronger interparticle bonds, transition elements have high melting and boiling points.***

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In moving along the period from left to right, the melting points of these metals first increase to maximum then gradually decrease towards the end of the period. Manganese and technitium possess anomalous melting points.

The trends of melting points of 3*d*, 4*d* and 5*d* transition metals are given in Fig. 11.2.

Reason. *The strength of interparticle bonds in transition elements is roughly related to the number of half-filled d- orbitals. In the beginning the number of half-filled d-orbitals increases till the middle of the period causing increase in strength of interparticle bonds. But thereafter, the pairing of electrons in d-orbitals occurs and the number of half- filled orbitals decrease which also causes decrease in melting points.*

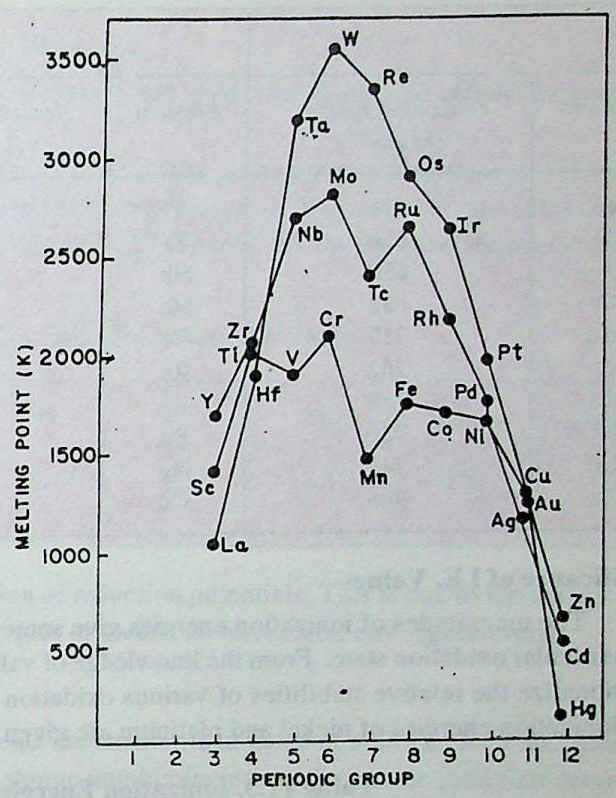

Fig. 11.2. Melting point of Transition metals.

3. Ionization Energy and Electrode Potentials

The ionization energies (*IE_1 values*) of transition elements are higher than those of *s*-block elements but lower than *p*-block elements. In a particular transition series, ionization energy increases gradually as we move from left to right. However, the relative difference of IE_1 values of any two consecutive *d*-block elements of particular period is much smaller than those of *s*- and *p*-block elements. *The increase in ionization energy is primarily due to increase in nuclear charge. As the transition elements involve the gradual filling of (n – 1) d-orbitals, the effect of increase in nuclear charge is partly cancelled by the increase in screening effect. Consequently, the increase in ionisation energy along the period of d-block element is very small.* The ionization energies of 3*d*-, 4*d*- and 5*d*-transition series are given in Table 11.2 and graphically represented in Fig. 11.3.

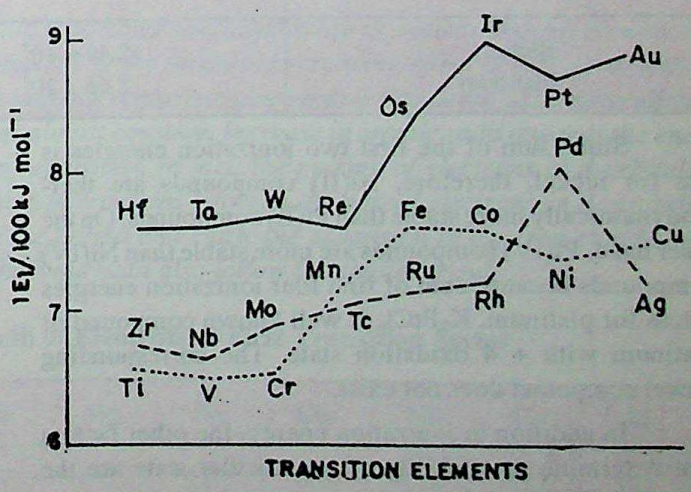

Fig. 11.3. Ionization energies of First, Second and Third transition series.

It may be noted that 5*d*-transition elements possess higher ionization energies than 3*d*- and 4*d*-transition elements. This is due to the greater effective nuclear charge in these elements because of the ineffective shielding of the nucleus by 4*f* electrons.

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Table 11.2. Ionization Energies of Transition Elements

I		*II*		*III*	
Element	*Ionization Energy ($kJ\ mol^{-1}$)*	*Element*	*Ionization Energy ($kJ\ mol^{-1}$)*	*Element*	*Ionization Energy ($kJ\ mol^{-1}$)*
Sc	631	Y	616	La	541
Ti	656	Zr	674	Hf	760
V	650	Nb	664	Ta	760
Cr	652	Mo	685	W	770
Mn	717	Tc	703	Re	759
Fe	762	Ru	711	Os	840
Co	758	Rh	720	Ir	900
Ni	736	Pd	804	Pt	870
Cu	745	Ag	731	Au	889
Zn	906	Cd	876	Hg	1007

Significance of I.E. Values

The magnitudes of ionization energies give some indication of the energy required to raise the metal to a particular oxidation state. From the knowledge of values of ionization energies of the metals it is possible to rationalize the relative stabilities of various oxidation states. For example, the sums of first two and first four ionization energies of nickel and platinum are given in Table 11.3.

Table 11.3. Ionization Energies of Nickel and Platinum

Element	*Sum of first two ionization energies $kJ\ mol^{-1}$*	*Sum of first four ionization energies $kJ\ mol^{-1}$*
Nickel	2.49×10^3	11.29×10^3
Platinum	2.66×10^3	9.36×10^3

Since sum of the first two ionization energies is less for nickel, therefore, Ni(II) compounds are thermodynamically more stable than Pt(II) compounds. On the other hand, Pt(IV) compounds are more stable than Ni(IV) compounds because sum of first four ionization energies is less for platinum. K_2PtCl_6 is well known compound of platinum with + 4 oxidation state. The corresponding nickel compound does not exist.

In addition to ionization energy, the other factors that determine the stability of a particular state are the enthalpy of sublimation of the metal and the lattice energy or the solvation energy. In order to understand this let us consider the flow chart given in Fig. 11.4.

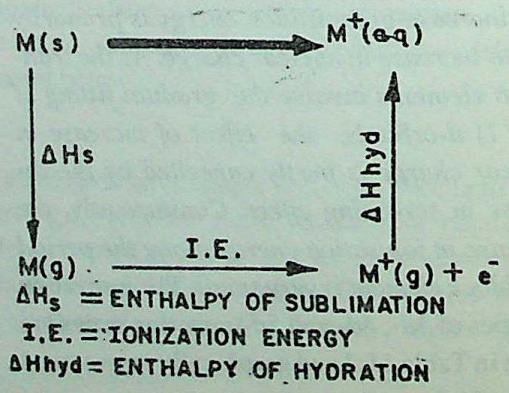

Fig. 11.4

From the given flow chart, it is clear that total enthalpy change, ΔH_T, for the process

$$M(s) \rightarrow M^+(aq) + e^-$$

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is equal to sum of enthalpy of sublimation of metal, ionization energy of metal and the enthalpy of hydration of the metal ion.

$$\Delta H_T = \Delta H_S + I.E. + \Delta H_{hyd.}$$

Smaller the value of ΔH_T, for a particular oxidation state of the metal, greater will be the stability of that oxidation state in aqueous solution.

The electrode potentials are measure of the value of ΔH_T. The lower the standard electrode potential ($E°_{red}$), the more stable is the oxidation state of the metal in the aqueous state. The electrode potentials can be determined experimentally. The standard electrode potentials (E°) for M^{2+}/M for first row transition metals are given in Table 11.4.

Table 11.4. Standard Electrode Potentials (M^{2+}/M)

Element	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
E° (M^{2+}/M) (V)	– 1.19	– 0.19	– 1.18	– 0.44	– 0.28	– 0.24	+ 0.34	– 0.76

It may be noted that there is no regular variation of reduction potentials. This is due to the reason that ionisation energies (IE_1 and IE_2) and sublimation energies of metals do not exhibit any regular trend.

4. Atomic and Ionic Radii

The atomic and ionic radii of transition elements are smaller than those of *s*-block elements. Among the elements of the particular transition series, as the atomic number increases, the atomic radii first decrease till the middle, becomes almost constant and then increases towards the end of the period. For example, the atomic radii of first transition series decreases from Sc to Cr, remains almost constant till Cu and then increases towards the end (Table 11.5).

Reason. *The decrease in size in the beginning is attributed to the increase in nuclear charge. However, the increased nuclear charge is partly cancelled by the increased screening effect of electrons in the d-orbitals of penultimate shell. When the increased nuclear charge and increased screening effect balance each other, the atomic radii become almost constant. Increase in atomic radii towards the end may be attributed to the electron-electron repulsions. In fact, the pairing of electrons in d-orbitals occurs after d^5 configuration. The repulsive interactions between the paired electrons in d-orbitals become very dominent towards the end of the period and cause the expansion of electron cloud and thus, resulting in increased atomic size. The ionic radii also follow the similar trend.*

Table 11.5. Atomic and Ionic Radii of Elements of First Transition Series

	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
Atomic Radii (pm)	144	132	122	117	117	117	116	115	117	125
Ionic Radii (pm)										
M^{2+}	—	90	88	84	80	76	74	72	72	74
M^{3+}	81	76	74	69	66	64	63	—	—	—

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The elements of second and third transition series belonging to a particular group have almost equal atomic radii (Table 11.6). This is because of lanthanide contraction (discussed in Section 11.5). For example, atomic radii of zirconium and hafnium are 160 pm and 159 pm respectively.

Table 11.6. Atomic Radii of Elements of Second and Third Transition Series

Element	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
Atomic Radii (pm)	180	160	160	146	136	134	134	137	144	154
Element	La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
Atomic Radii (pm)	187	159	146	139	137	135	136	138	144	157

5. Oxidation States

All transition metals exhibit a great variety of oxidation states. The oxidation states of transition elements are listed in Table 11.7. The less common and unstable oxidation states are given in the parentheses. The stability of a particular oxidation state depends upon the nature of the element with which the transition metal forms the compound. The highest oxidation states are found in compounds of fluorine and oxygen. This is due to the high electronegativity values and small size of fluorine and oxygen.

The variable oxidation states of transition elements are due to the participation of ns and (n – 1) d-electrons in bonding. The lower oxidation state is generally, exhibited when ns-electrons participate in bonding and higher oxidation states are shown when ns as well as (n – 1) d-electrons take part in bonding.

Some noteworthy features of oxidation states of the transition elements are :

1. *In each group, the highest oxidation state increases with increase in atomic number, reaches a maximum in the middle and then starts decreasing.* For example, for the first transition series the maximum oxidation state is shown by manganese.
2. *For the elements of first transition series* (except scandium) + 2 *oxidation state is the most common oxidation sate.* This oxidation state arises due to the loss of 4*s*-electrons.

Table 11.7. Different Oxidation States of Transition Metals

Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn
+ 3	(+ 2) + 3 + 4	+ 2 + 3 + 4 + 5	+ 2 + 3 (+ 4) (+ 5) + 6	+ 2 (+ 3) + 4 (+ 6) + 7	+ 2 + 3 (+ 4)	+ 2 + 3 (+ 6)	+ 2 (+ 3) (+ 4)	+ 1 + 2	+ 2

Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd
+ 3	(+ 3) + 4	(+ 2) (+ 3) (+ 4) + 5	(+ 2) + 3 + 4 + 5 + 6	+ 4 (+ 5) + 7	+ 2 + 3 + 4 (+ 5) (+ 6) (+ 7) (+ 8)	+ 3 + 4 (+ 6)	+ 2 (+ 3) + 4	+ 1 (+ 2) (+ 3)	+ 2

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La	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg
+ 3	(+ 3) + 4	(+ 2) (+ 3) (+ 4) + 5	+ 2 (+ 3) + 4 + 5 + 6	+ 3 + 4 (+ 5) (+ 6) + 7	(+ 2) (+ 3) + 4 + 6 + 8	(+ 2) + 3 + 4 (+ 6)	+ 2 (+ 3) + 4 (+ 5) (+ 6)	+ 1 + 3	+ 1 + 2

Note. Less common and unstable oxidation states states are given in parentheses.

3. *The transition elements in lower oxidation states (+ 2 and + 3) generally form ionic bonds. In higher oxidation states, the bonds formed are essentially covalent.* For example, in chromate ion (CrO_4^{2-}), the bonds formed between chromium and oxygen are covalent.
4. *The highest oxidation state shown by any transition metal is + 8.* For example, ruthenium and osmium show highest oxidation states of + 8 in some of their compounds.
5. *Some transition metals also show oxidation state of zero in their compounds.* $[Ni(CO)_4]$ and $[Fe(CO)_5]$ are common examples. (For details refer Unit 12).

6. Complex Formation

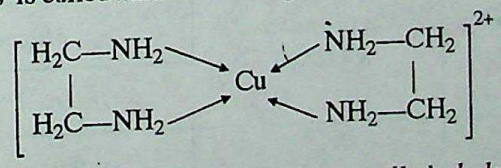
In contrast to the representative elements, transition elements form many co-ordination complexes. Their tendency to form complexes is attributed to the following reasons :

1. *Small size and high charge density of the ions of transition metals.*
2. *Presence of vacant orbitals of appropriate energy which can accept lone pairs of electrons donated by other groups (ligands).*

The number of electron pairs accepted by the transition metal ion is called **co-ordination number** of the transition element. Some examples of complexes of transition elements are given below :

$[Cu(NH_3)_4]^{2+}$ $[Ni(CN)_4]^{2-}$
$[Ag(NH_3)_2]^{+}$ $[Ni(CO)_4]$
$[Cr(NH_3)_6]^{3+}$ $[Fe[CN)_6]^{4-}$

If the ligand is attached to the central atom only at one point, the ligand is called *monodentate ligand.* NH_3, CN^- and CO are the examples of monodentate ligands. A ligand which is attached to the central atom through more than one atoms is called *multidentate ligand.* For example, ethylenediamine is bidentate ligand.



The complexes formed by multidentate ligands are called *chelates.* We shall study more about these complexes in Unit 12.

Coloured Complexes

The compounds of transition elements are usually coloured. The colour of these complexes is due to absorption of some radiation from visible light, which is used in promoting an electron from one of the *d*-orbitals to another. This can be explained as under :

The d-orbitals in the transition elements do not have same energy in their complexes. Under the influence of the ligands attached, the d-orbitals split into two sets of orbitals having slightly different energies.

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In the transition elements which have partly filled d-orbitals, the transition of electron can take place from one of the lower d-orbitals to some higher d-orbital within the same sub-shell. The energy required for this transition falls in the visible region. So when white light falls on these complexes they absorb a particular colour from the radiation for the promotion of electron and the remaining colours are emitted. The colour of the complex is due to this emitted radiation. For example, cupric salts are bluish green due to absorption of red light. Ti^{3+} salts appear purple due to absorption of yellow light.

Zn^{2+} and Ti^{4+} salts are white because they do not absorb any radiation in the visible region. In these compounds, *d-d* transitions are not possible because in Zn^{2+} all the *d*-orbitals are fully-filled whereas in Ti^{4+} all the *d*-orbitals are vacant. The colours of some transition metal complexes are given in Table 11.8.

Table 11.8. Colours of Some Complexes

Complex	*Colour*
$[Cu(H_2O)_6]^{2+}$	Light blue
$[Co(H_2O)_6]^{2+}$	Pink
$[Ni(H_2O)_6]^{2+}$	Green
$[Cr(H_2O)_6]^{3+}$	Violet
$[Ni(NH_3)_6]^{2+}$	Blue

7. Magnetic Properties

The substances, which contain some species (atoms, ions or molecules) with unpaired electrons in their orbitals, behave as *paramagnetic* substances. Such substances are weakly attracted by magnetic field. On the other hand, the substances whose constituent particles do not contain any unpaired electrons are repelled by magnetic field and are called *diamagnetic.*

The transition metal ions generally contain one or more unpaired electrons in them and hence their complexes are generally paramagnetic. The paramagnetic character increases with increase in number of unpaired electrons. The paramagnetism is expressed in terms of magnetic moment. The magnetic moments of some ionic species belonging to first transition series are given in Table 11.9.

Table 11.9. Magnetic Moments of Some Ionic Species

Ion	*Outer electronic configuration*	*No. of unpaired electrons*	*Magnetic moment (BM)*	
			Observed	*Calculated*
Sc^{3+}	$3d^0$	0	0.0	0
Ti^{3+}	d^1	1	1.75	1.73
V^{3+}	d^2	2	2.76	2.83
Cr^{3+}	d^3	3	3.80	3.87
Mn^{2+}	d^5	5	5.96	5.92
Fe^{2+}	d^6	4	5.10	4.89
Co^{2+}	d^7	3	4.4 – 5.2	3.87
Ni^{2+}	d^8	2	2.9 – 3.4	2.83
Cu^{2+}	d^9	1	1.8 – 2.2	1.73
Zn^{2+}	d^{10}	0	0.0	0.0

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The magnetic moment is related to the number of unpaired electrons according to the following relation :

Magnetic moment, $\mu = \sqrt{n(n+2)}$ *B.M.*

where n is the number of unpaired electrons and *B.M.* stands for *Bohr magneton*, a unit of magnetic moment.

$$1\ BM = \frac{eh}{4\pi mC}$$

where e is electronic charge, m is mass of electron, h is Planck's constant and C is velocity of light.

It may be noted that total magnetic moment depends upon spin magnetic moment as well as orbital magnetic moment. However, in calculated values of magnetic moment, the contribution of orbital magnetic moment (being insignificant) has been neglected. That is why, they differ slightly from the observed values given in Table 11.9.

8. Catalytic Properties

Many transition metals and their compounds are known to act as catalysts. For example, finely divided iron acts as catalyst in the manufacture of ammonia by Haber process, vanadium pentoxide (V_2O_5) or platinum act as catalyst for the oxidation of SO_2 to SO_3 in contact process, ferrous, sulphate and hydrogen peroxide (Fenton's reagent) are used for the oxidation of alcohols to aldehydes.

The catalytic activity of transition metals is attributed to the following reasons :

1. *Because of their variable valencies transition metals sometimes form unstable intermediate compounds and provide a new path with lower activation energy for the reaction.*

For example, during the conversion of SO_2 to SO_3, V_2O_5 adsorbs SO_2 molecule on its surface and gives oxygen to it to form SO_3 and V_2O_4. V_2O_4 then reacts with oxygen to form V_2O_5.

$$V_2O_5 + SO_2 \longrightarrow SO_3 + \underset{\text{Divanadium tetroxide}}{V_2O_4}$$

$$V_2O_4 + \tfrac{1}{2}O_2 \longrightarrow V_2O_5$$

2. *In some cases transition metals provide a suitable surface of the reaction to take place. The reactants are adsorbed on the surface of the catalyst where reaction occurs.*

9. Formation of Alloys

The *d*-block elements have almost similar atomic sizes. Therefore, these elements can mutually substitute their positions in their crystal lattices. In this way, many alloys are possible between transition metals. Brass, bronze and various types of steels are examples of this type of alloys. The alloys so formed are relatively hard and possess higher melting points.

10. Interstitial Compounds

The transition elements are capable of entrapping smaller atoms of other elements such as H, C and N in the interstitial sites in their crystal lattices. These trapped atoms get bonded to the atoms of transition elements. The presence of these atoms results in decrease in malleability and ductility of the metals, but increases their tensile strength. For example, steel and cast iron are hard due to the presence of trapped carbon in the interstitial spaces.

REVIEW QUESTIONS

11.1. Name the first and the last element in the second transition series.

11.2. Name the *d*-block elements which do not have partially filled *d*-orbitals in their atoms or in their simple ions.

11.3. Name the lightest and the heaviest elements (in terms of density) in the transition elements.

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11.4. What is the general electronic configuration of transition elements ?

11.5. Which element among transition elements has (*i*) the lowest melting point (*ii*) the highest melting point ?

11.6. Name the three factors which determine the stability of a particular oxidation state.

11.7. What is the most common oxidation state of first transition series ?

11.8. Which of the following ions would form white complexes ?

$$Cu^{2+}, Zn^{2+}, Ti^{3+}, Ti^{4+}, Cd^{2+}.$$

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11.3. GENERAL PROPERTIES OF FIRST ROW TRANSITION METAL COMPOUNDS

The transition metals react with non-metals such as oxygen, nitrogen, phosphorus, halogens, sulphur and carbon to form binary compounds. Some of these compounds possess immense industrial importance.

1. Oxides

The elements of first transition series form variety of oxides of different oxidation states having general formulae MO, M_2O_3, M_3O_6, MO_2, MO_3. These oxides are generally formed by heating the metal with oxygen at high temperature. These oxides have been listed in Table 11.10. These oxides exhibit acidic, basic and amphoteric behaviour.

Some of the characteristic features of these oxides are given below :

(*i*) In general, oxides are **basic** when the metal is in lower oxidation state and they are **acidic** if the metal is in higher oxidation state.

(*ii*) The oxides are generally amphoteric if the metal is in intermediate oxidation state.

For example, the oxides of Mn have the behaviour as

Oxide :	**MnO**	**Mn_2O_3**	**Mn_3O_4**	**MnO_2**	**Mn_2O_7**
O.N. of Mn :	+ 2	+ 3	+ 8/3	+ 4	+ 7
	Basic		Amphoteric		Acidic

Basic character DECREASES
and Acid Character INCREASES

(*iii*) The basic and amphoteric oxides generally dissolve in non-oxidising acids like HCl to form hexa-aquo ions $[M(H_2O)_6]^{n+}$.

(*iv*) Some of these oxides dissolve in acids or bases to form oxometallic salts such as potassium chromate, potassium dichromate and potassium permanganate, etc.

Table 11.10. Oxides of First Row Transition Metals

Sc	ScO_3 (*b*)
Ti	TiO (*b*), Ti_2O_2 (*b*), TiO_2 (*c*)
V	VO (*b*), V_2O_3 (*b*), VO_2 (*c*), V_2O_5 (*a*)
Cr	CrO (*b*), Cr_2O_3 (*c*), CrO_2 (*c*), CrO_3 (*a*)
Mn	MnO (*b*), Mn_2O_3 (*b*), Mn_3O_4 (*c*), MnO_2 (*c*), Mn_2O_7 (*a*)

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Fe	FeO (*b*), **Fe_2O_3** (*c*), **Fe_3O_4** (*b*)
Co	CoO (*b*)
Ni	NiO (*b*)
Cu	Cu_2O (*b*), CuO (*c*)
Zn	ZnO (*c*)

Notes. (*i*) The stable oxides have been indicated by bold letters.

(*ii*) The acidic, basic or amphoteric nature of oxide is indicated by writing (*a*), (*b*) or (*c*) respectively after the oxide.

Let us discuss two of the important oxometallic salts namely ; *potassium dichromate* and *potassium permanganate.*

Potassium Dichromate ($K_2Cr_2O_7$)

Potassium dichromate is prepared from *chromite* ore ($FeCr_2O_4$). The various steps involved are :

1. *Preparation of sodium chromate.* The powdered ore is heated with molten alkali in the presence of air in a reverberatory furnace to produce sodium chromate.

$$4FeCr_2O_4 + 16NaOH + 7O_2 \longrightarrow 8Na_2CrO_4 + 2Fe_2O_3 + 8H_2O$$

2. *Conversion of sodium chromate into sodium dichromate.* Sodium chromate is extracted with water and acidified with sulphuric acid to get sodium dichromate.

$$2Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$$

On cooling, sodium sulphate separates out as $Na_2SO_4.10H_2O$ and the solution contains sodium dichromate in it.

3. *Conversion of sodium dichromate into potassium dichromate.* The solution containing sodium dichromate is treated with potassium chloride.

$$Na_2Cr_2O_7 + 2KCl \longrightarrow K_2Cr_2O_7 + 2NaCl$$

Sodium chloride being least soluble separates out and is removed by filtration. On cooling, potassium dichromate crystallizes out in the form of *orange crystals*. Potassium dichromate is *fairly soluble* in water.

The structure of dichromate ion is shown below in Fig. 11.5. It consists of two tetrahedra sharing an oxygen atom at the common corner.

The dichromate ion ($Cr_2O_7^{2-}$) and chromate ion (CrO_4^{2-}) exist in equilibrium with each other at a pH of about 4. They are interconvertible by changing the pH. The chromate ions on addition of acid change into dichromate ion while the dichromate ions on addition of alkali change into chromate ion.

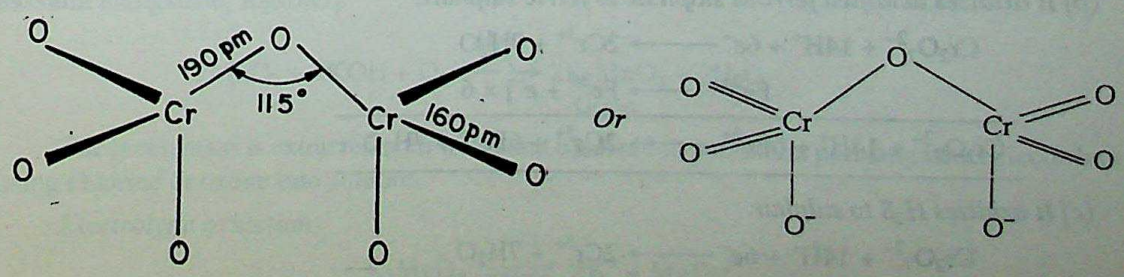

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Fig. 11.5. Dichromate ion ($Cr_2O_7^{2-}$).

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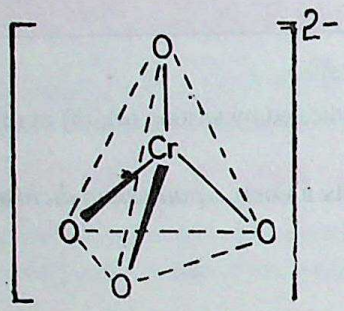
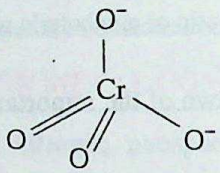
$$\underset{\substack{\text{Chromate}\\\text{(yellow)}}}{2CrO_4^{2-}} + 2H^+ \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} \underset{\substack{\text{Hydrogen}\\\text{chromate}}}{2HCrO_4^-} \underset{\text{Alkali}}{\overset{\text{Acid}}{\rightleftharpoons}} \underset{\substack{\text{Dichromate}\\\text{(orange)}}}{Cr_2O_7^{2-}} + 2H_2O$$

The chromate ion has tetrahedral structure as shown below :



CHROMATE ION
(CrO_4^{2-})

Or



Properties of Potassium Dichromate

1. It is an orange crystalline solid with melting point 670 K.
2. It is appreciably soluble in hot water but moderately soluble in cold water.
3. ***Action of heat.*** On heating $K_2Cr_2O_7$ decomposes to give potassium chromate and chromic oxide.

$$4K_2Cr_2O_7 \xrightarrow{\Delta} 4K_2CrO_4 + 2Cr_2O_3 + 3O_2$$

4. ***Oxidizing properties.*** It acts as strong oxidizing agent in acidic medium.

$$K_2Cr_2O_7 + 4H_2SO_4 \longrightarrow K_2SO_4 + Cr_2(SO_4)_3 + 4H_2O + 3[O]$$

or $$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O \qquad [E^\circ = 1.31\ V]$$

Since $Cr_2O_7^{2-}$ ions take up electrons so they get reduced and act as oxidizing agent. Some of the oxidizing reactions of $K_2Cr_2O_7$ are given below :

(*a*) *It oxidizes iodides to iodine.*

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$2I^- \longrightarrow I_2 + 2e^-] \times 3$$
$$\overline{Cr_2O_7^{2-} + 6I^- + 14H^+ \longrightarrow 2Cr^{3+} + 3I_2 + 7H_2O}$$

(*b*) *It oxidizes acidified ferrous sulphate to ferric sulphate.*

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$Fe^{2+} \longrightarrow Fe^{3+} + e^-] \times 6$$
$$\overline{Cr_2O_7^{2-} + 14H^+ + 6Fe^{2+} \longrightarrow 2Cr^{3+} + 6Fe^{3+} + 7H_2O}$$

(*c*) *It oxidizes H_2S to sulphur.*

$$Cr_2O_7^{2-} + 14H^+ + 6e^- \longrightarrow 2Cr^{3+} + 7H_2O$$
$$H_2S \longrightarrow S + 2H^+ + 2e^-] \times 3$$
$$\overline{Cr_2O_7^{2-} + 3H_2S + 8H^+ \longrightarrow 2Cr^{3+} + 3S + 7H_2O}$$

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Similarly, it oxidizes sulphites to sulphates, chlorides to chlorine, nitrites to nitrates, thiosulphates to sulphates and sulphur and stannous salts (Sn^{2+}) to stannic salts (Sn^{4+}) according the equation given below.

$$\underset{\text{Sulphate}}{3SO_3^{2-}} + Cr_2O_7^{2-} + 8H^+ \longrightarrow \underset{\text{Sulphate}}{3SO_4^{2-}} + 2Cr^{3+} + 4H_2O$$

$$\underset{\text{Chloride}}{6Cl^-} + Cr_2O_7^{2-} + 14H^+ \longrightarrow \underset{\text{Chlorine}}{3Cl_2} + 2Cr^{3+} + 7H_2O$$

$$\underset{\text{Nitrate}}{3NO_2^-} + Cr_2O_7^{2-} + 8H^+ \longrightarrow \underset{\text{Nitrate}}{3NO_3^-} + 2Cr^{3+} + 4H_2O$$

$$\underset{\text{Thiosulphate}}{3S_2O_3^{2-}} + Cr_2O_7^{2-} + 8H^+ \longrightarrow \underset{\text{Sulphate}}{3SO_4^{2-}} + 3S + 2Cr^{3+} + 4H_2O$$

$$\underset{\text{Stannous}}{3Sn^{2+}} + Cr_2O_7^{2-} + 14H^+ \longrightarrow \underset{\text{Stannic}}{3Sn^{4+}} + 2Cr^{3+} + 7H_2O$$

5. ***Chromyl chloride test.*** When any chloride is heated with $K_2Cr_2O_7$ and conc. H_2SO_4 orange red fumes of chromyl chloride (CrO_2Cl_2) are formed.

$$K_2Cr_2O_7 + 4NaCl + 6H_2SO_4 \longrightarrow 2KHSO_4 + 4NaHSO_4 + 2CrO_2Cl_2 + 3H_2O$$

6. ***Reaction with H_2O_2.*** Acidified solution dichromate ions forms a deep blue colour with H_2O_2 due to the formation of $[CrO(O_2)_2]$

$$Cr_2O_7^{2-} + 4H_2O_2 + 2H^+ \longrightarrow 2CrO_5 + 5H_2O$$

The blue colour fades away gradually due to decomposition of CrO_5 into Cr^{3+} ions and oxygen.

Use of Potassium Dichromate :

(*i*) For the volumetric estimation of ferrous salts, iodides and sulphites.

(*ii*) For preparation of other chromium compounds such as chrome alum, $K_2SO_4.Cr_2(SO_4)_3.24H_2O$, chrome yellow ($PbCrO_4$) and chrome red ($PbCrO_4PbO$).

(*iii*) Used in photography for hardening of gelatin film.

(*iv*) In dyeing for providing $Cr(OH)_3$ as a mordant.

(*v*) Chromic acid mixture used for cleaning glassware, consists of $K_2Cr_2O_7$ and conc. H_2SO_4.

(*vi*) Potassium dichromate is used in chrome tanning in leather industry .

(*vii*) It is used as an oxidizing agent.

Potassium Permanganate ($KMnO_4$)

Potassium permanganate is prepared from *pyrolusite* (MnO_2). Pyrolusite is fused with KOH in the presence of atmospheric oxygen or an oxidizing agent like potassium nitrate or potassium chlorate to give potassium manganate, K_2MnO_4.

$$2MnO_2 + 4KOH + O_2 \xrightarrow{\text{Heat}} \underset{\text{Green}}{2K_2MnO_4} + 2H_2O$$

The green mass is extracted with water and oxidized to potassium permanganate, electrolytically or by passing chlorine or ozone into solution.

Electrolytic oxidation

$$K_2MnO_4 \rightleftharpoons 2K^+ + MnO_4^{2-}$$

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$$H_2O \rightleftharpoons H^+ + OH^-$$

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During electrolysis manganate ions are oxidized to permanganate *at anode*

$$\underset{\text{Green}}{MnO_4^{2-}} \longrightarrow \underset{\text{Purple}}{MnO_4^- + e^-}$$

At cathode hydrogen gas is liberated

$$2H_2O + 2e^- \longrightarrow H_2 + 2OH^-$$

Oxidation by chlorine

$$2K_2MnO_4 + Cl_2 \longrightarrow 2KMnO_4 + 2KCl$$

or $$2MnO_4^{2-} + Cl_2 \longrightarrow 2MnO_4^- + 2Cl^-$$

Oxidation by ozone

$$2K_2MnO_4 + O_3 + H_2O \longrightarrow 2KMnO_4 + 2KOH + O_2$$

or $$2MnO_4^{2-} + O_3 + H_2O \longrightarrow 2MnO_4^{2-} + 2OH^- + O_2$$

As a result of oxidation, the green colour of solution changes into purple. The purple solution containing $KMnO_4$ is concentrated by evaporation which on cooling gives crystals of $KMnO_4$.

Properties of Potassium Permanganate

Potassium permanganate is violet crystalline solid having m.p. 523 K. It is soluble in water and its aqueous solution is purple in colour.

1. ***Effect of heat.*** On heating potassium permanganate changes into manganate and oxygen gas is evolved.

$$2KMnO_4 \longrightarrow K_2MnO_4 + MnO_2 + O_2$$

2. ***Effect of alkalies.*** On heating with alkalies, potassium permanganate changes into manganate and oxygen gas is evolved.

$$4KMnO_4 + 4KOH \longrightarrow 4K_2MnO_4 + 2H_2O + O_2$$

3. ***Oxidizing properties.*** $KMnO_4$ acts as a very powerful oxidizing agent in acidic, neutral and alkaline media. The equations representing oxidation in these media are given below :

In acidic medium

$$2KMnO_4 + 3H_2SO_4 \longrightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + 5[O]$$

or $$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \qquad [E^\circ = +1.51\ V]$$

In neutral or alkaline medium

$$2KMnO_4 + H_2O \longrightarrow 2KOH + 2MnO_2 + 3[O]$$

or $$MnO_4^- + 2H_2O + 3e^- \longrightarrow MnO_2 + 4OH^- \qquad [E^\circ = +1.23\ V]$$

In acidic medium potassium permanganate oxidizes :

(*a*) *Ferrous salts to ferric salts*

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O$$

$$[Fe^{2+} \longrightarrow Fe^{3+} + e^-\ ] \times 5$$

$$MnO_4^- + 5Fe^{2+} + 8H^+ \longrightarrow Mn^{2+} + 5Fe^{3+} + 4H_2O$$

(*b*) *Oxalates to CO_2*

$$[MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O\ ] \times 2$$

$$[C_2O_4^{2-} \longrightarrow 2CO_2 + 2e^-\ ] \times 5$$

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$$2MnO_4^- + 5C_2O_4^{2-} + 16H^+ \longrightarrow 2Mn^{2+} + 10CO_2 + 8H_2O$$

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(c) *Iodides to iodine*

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O \quad] \times 2$$
$$2I^- \longrightarrow I_2 + 2e^- \quad] \times 5$$
$$10I^- + 2MnO_4^- + 16H^+ \longrightarrow 2Mn^{2+} + 5I_2 + 8H_2O$$

(d) *Sulphites to sulphates*

$$MnO_4^- + 8H^+ + 5e^- \longrightarrow Mn^{2+} + 4H_2O] \times 2$$
$$SO_3^{2-} + H_2O \longrightarrow SO_4^{2-} + 2H^+ + 2e^-] \times 5$$
$$5SO_3^{2-} + 2MnO_4^- + 6H^+ \longrightarrow 2Mn^{2+} + 5SO_4^{2-} + 3H_2O$$

In alkaline medium it oxidizes *iodides to iodates* :

$$I^- + 2MnO_4^- + H_2O \longrightarrow IO_3^- + 2MnO_2 + 2OH^-$$

Use of Potassium permanganate :

(*i*) As an oxidizing agent in the laboratory and industry.

(*ii*) For volumetric estimation of ferrous salts, oxalates and other reducing agents.

(*iii*) For qualitative detection of halides, oxalates, tartrates, sulphites, etc.

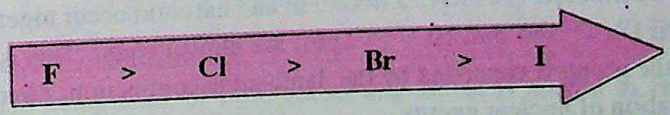
(*iv*) As dis-infectant for water.

(*v*) In dry cells.

(*vi*) As laboratory reagent (Baeyer's reagent).

2. Halides

Transition metals react with halogens at high temperatures to form halides. These reactions have very high activation energies, therefore, high temperatures are required to start these reactions. However, once the reaction starts, the heat liberated is sufficient to sustain the reaction. The order of reactivity of different halogens decreases as :



—*Order of reactivity*

Fluorides are usually ionic whereas chlorides, bromides and iodides are predominantly covalent. The covalent character increases with increase in atomic mass of the halogen. For example, CuF_2 is ionic while $CuCl_2$ and $CuBr_2$ are covalent consisting of infinite chains. Co-ordination number of copper in these compounds is six as shown in Fig. 11.6.

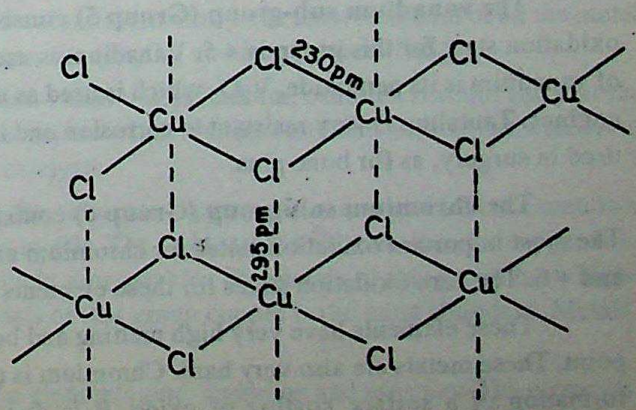


Fig. 11.6. Structure of Copper (II) chloride.

Fluorine brings about highest oxidation state of the metal. This is due to its small size and high electronegativity. Halides of metals in higher oxidation states are relatively unstable and get hydrolysed easily. For example,

$$TiCl_4 + 2H_2O \longrightarrow TiO_2 + 4HCl$$

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3. Sulphides

Sulphides of transition metals are prepared either by direct combination of sulphur with metals or by the reaction of H_2S or Na_2S with the solution of their salts. In sulphides, the oxidation state of metal is generally low because sulphur is a weak oxidising agent. These sulphides are generally coloured or black. For example, NiS, CoS and CuS are black, MnS is light pink, and CdS is yellow. They are insoluble in water.

REVIEW QUESTIONS

11.9. What is the structure of chromate ion ?

11.10. Which of following oxides are acidic and which are basic

Mn_2O_7, MnO, CrO_3, VO, Cu_2O, V_2O_5.

11.11. H_2S gas is passed through an acidified solution of $K_2Cr_2O_7$. The solution becomes milky. How do you explain it ?

11.12. What happens when KI solution is added to

(*i*) alkaline solution of $KMnO_4$ (*ii*) acidified solution of $KMnO_4$?

11.13. What is the chemical formula of chromyl chloride ?

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11.4. SOME GENERAL GROUP TRENDS IN THE CHEMISTRY OF TRANSITION METALS

Group 4, the **titanium sub-group** of transition metals consists of the elements *titanium, zirconium and hafnium.* The most important member of this group is titanium. It is extremely strong, has high melting point and is resistant to corrosion. It is in great demand as structural material. Zirconium and hafnium are silvery white metals. The most stable oxidation state for the elements of this class is + 4. Titanium also possesses + 3 oxidation state. The typical compounds of these elements are chlorides, $TiCl_4$, $ZrCl_4$, $HfCl_4$ and oxides TiO_2, ZrO_2 and HfO_2, ZrO_2 is a refractory material. Titanium is quite abundant in nature and mainly occurs as oxide ores, rutile (TiO_2) and ilmenite ($FeTiO_3$). Zirconium and hafnium occur together and exhibit similar properties. Their atomic radii (Zr = 160 pm, Hf = 159 pm) are almost equal. This is due to the reason that usual increase in size down the group is cencelled by the lanthanide contraction. Zirconium and hafnium are both important for the generation of nuclear energy.

The **vanadium sub-group (Group 5)** consists of *vanadium, niobium* and *tantalum.* The most stable oxidation state for this group is + 5. Vanadium is used as an additive to steel. The most important compound of vanadium is its pentoxide, V_2O_5 which is used as catalyst in many reactions. Niobium alloys are used in jet engines. Tantalum is very resistant to corrosion and is used for making apparatus in chemical plants. It is also used in surgery, as for bone pins.

The **chromium sub-group (Group 6)** contains the elements, *chromium, molybdenum* and *tungsten.* The most important oxidation states for chromium are + 3 and + 6, and for molybdenum and tungsten as + 5 and + 6. The zero oxidation states for these elements arise in metal carbonyls such as $Cr(CO)_6$.

These elements have very high melting and boiling points. Tungsten is the metal with highest melting point. These metals are also very hard. Chromium is unreactive or passive at low temperatures because of the formation of a surface coating of oxide. It is due to this passive behaviour that chromium is used for electroplating iron to prevent rusting.

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These elements are relatively abundant, chromium being the most abundant among these metals. The common ore of chromium is *Chromite* ($FeCr_2O_4$). Molybdenum occurs as molybdenite (MoS_2) and tungsten occurs as tungstates such as wolframite, $FeWO_4.MnWO_4$.

The metals of this group are very useful. Chromium is used in many ferrous alloys such as stainless steel, chrome steel, etc. It is also used for electroplating iron or some other metal to prevent corrosion. $K_2Cr_2O_7$ is a very important useful compound of chromium.

Molybdenum and tungsten form very hard alloys with steel and are used in making cutting tools. Tungsten is also used as filament in electric bulbs. Molybdenum disulphide, MoS_2 acts as lubricant because it has layer lattice.

Group 7, the manganese sub-group, consists of the elements *manganese, technitium* and *rhenium.* The elements exhibit all the oxidation states from 0 to + 7, the most important being + 2, + 4 and + 7 for manganese and + 4 and + 7 for technitium and rhenium.

Among the elements of this group, only manganese is quite abundant (being tenth most abundant element). Manganese occurs in the form of oxide ores such as *pyrolusite* (MnO_2), *braunite* (Mn_2O_3) and *hausmanite* (Mn_3O_4). Technetium does not occur in nature and is the first man-made element. It is radioactive and has only recently been studied. Rhenium is also a very rare element and occurs in small traces in ores of molybdenum.

The elements of this group have quite high melting and boiling points.

Manganese is obtained from its oxide ores by reduction with carbon or aluminium. Manganese metal does not have any use as such but is used in the manufacture of alloys such as ferromanganese (Fe + Mn) and manganese bronze (Mn + Cu + Zn). $KMnO_4$ is an important compound of Mn which is used as oxidizing agent and finds so many other applications. Manganese dioxide is used as catalyst. Rhenium is used in electronic filaments, high temperature thermocouples and in flash bulbs.

The metals of groups 8, 9 and 10 are known as **iron group** metals. These elements are :

Group →	8	9	10
	Iron *Ruthenium* *Osmium*	*Cobalt* *Rhodium* *Iridium*	*Nickel* *Palladium* *Platinum*

The first triad comprising of iron, cobalt and nickel is known as ferrous metals. These metals are ferromagnetic. Iron and cobalt exhibit oxidation states of + 3 and + 2 in their compounds while nickel compounds are generally in the + 2 oxidation state. After aluminium, iron is the most abundant of all the metals. The important ores of iron are *haematite* (Fe_2O_3), *magnetite* (Fe_3O_4) and *iron pyrites* (FeS_2).

The elements of second and third triad, ruthenium, rhodium, palladium, osmium, iridium and platinum are collectively known as *platinum metals*. These elements are relatively less abundant and exhibit wider range of oxidation states. They are inert and serve as good catalysts.

The **copper sub-group (group 11)** includes the elements *copper, silver* and *gold.* These metals are known as *coinage metals.* They form alloys with many metals. The most stable oxidation state for copper is + 2. For silver and gold the oxidation state of + 1 is relatively more stable. The metals of this group have highest electrical and thermal conductivities. Among the metals of this group copper is the most abundant. Metals of this group occur in combined as well as free state.

The **zinc sub-group (group 12)** consists of the elements *zinc, cadmium* and *mercury.* The elements of this group show none of the characteristic properties of transition metals. The metals of this group are

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moderately electropositive and exhibit an oxidation state of + 2. Since their ionization energy is very high none of these metals possess oxidation state of higher than + 2. Mercury, due to metal-metal bond also shows a formal oxidation state of + 1. The elements of this group are diamagnetic. Zinc is moderately abundant while cadmium and mercury are less abundant. However, all these elements are well known because of the existence of concentrated deposits and simple metallurgy. Mercury is the only metal which exists as liquid at room temperature.

REVIEW QUESTIONS

11.14. Name two ores of titanium.

11.15. Give two uses of vanadium.

11.16. Name the coinage metals.

11.17. What is oxidation state exhibited by group 12 elements ?

11.18. Name the transition element which exists as liquid at room temperature.

11.19. Name the iron group metals.

11.20. Explain why zinc, cadmium and mercury do not exhibit characteristic properties of metals.

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11.5. LANTHANIDES AND ACTINIDES

The *f*-block elements consist of two series of inner transition elements *i.e., lanthanides* and *actinides*. They are also called rare earth elements. **Lanthanides** involve the filling of 4*f*-orbitals while **actinides** involve the filling of 5*f*-orbitals in their atoms. These *f*-orbitals belong to the shell third from the outer shell. This factor accounts for some characteristic properties of these elements. The members of lanthanide and actinide series are listed in Table 11.11 and Table 11.12 respectively. Lanthanum, the first member of lanthanides has the configuration of $5d^1 6s^2$ and next member cerium, has $4f^2 6s^2$ while the next element praseodymium has the configuration $4f^3 6s^2$. Although lanthanum itself does not possess any 4*f* electrons, it is customary to include this element in the series. The electronic configurations of the elements with fully filled (f^{14}) and half-filled (f^7) *f*-orbitals are relatively more stable. The extra stability of half-filled orbitals is seen in the elements europium ($4f^7 6s^2$) and gadolinium ($4f^7 5d^1 6s^2$). The element ytterbium has fully-filled *f*-orbitals with the configuration $4f^{14} 6s^2$ and the extra electron in lutetium goes in 5*d* orbitals ($4f^{14} 5d^1 6s^2$). So except for lanthanum, gadolinium and lutetium which have a single electron in 5*d* orbitals the lanthanides do not have electrons in the 5*d* orbitals.

Table 11.11. Electronic Configuration of Lanthanides

Element	*Symbol*	*Atomic number*	*Configuration*
Lanthanum	La	57	$5d^1 6s^2$
Cerium	Ce	58	$4f^2 6s^2$
Praseodymium	Pr	59	$4f^3 6s^2$
Neodymium	Nd	60	$4f^4 6s^2$
Promethium	Pm	61	$4f^5 6s^2$
Samarium	Sm	62	$4f^6 6s^2$
Europium	Eu	63	$4f^7 6s^2$

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Element	*Symbol*	*Atomic number*	*Configuration*
Gadolinium	Gd	64	$4f^7\ 5d^1\ 6s^2$
Terbium	Tb	65	$4f^9\ 6s^2$
Dysprosium	Dy	66	$4f^{10}\ 6s^2$
Holmium	Ho	67	$4f^{11}\ 6s^2$
Erbium	Er	68	$4f^{12}\ 6s^2$
Thulium	Tm	69	$4f^{13}\ 6s^2$
Ytterbium	Yb	70	$4f^{14}\ 6s^2$
Lutetium	Lu	71	$4f^{14}\ 5d^1\ 6s^2$

Table 11.12. Electronic Configuration of Actinides

Element	*Symbol*	*Atomic number*	*Configuration*
Actinium	Ac	89	$6d^1\ 7s^2$
Thorium	Th	90	$6d^2\ 7s^2$
Protactinium	Pa	91	$5f^2\ 6d^1\ 7s^2$
Uranium	U	92	$5f^3\ 6d^1\ 7s^2$
Neptunium	Np	93	$5f^4\ 6d^1\ 7s^2$
Plutonium	Pu	94	$5f^6\ 7s^2$
Americium	Am	95	$5f^7\ 7s^2$
Curium	Cm	96	$5f^7\ 6d^1\ 7s^2$
Berkelium	Bk	97	$5f^8\ 6d^1\ 7s^2$
Californium	Cf	98	$5f^{10}\ 7s^2$
Einsteinium	Es	99	$5f^{11}\ 7s^2$
Fermium	Fm	100	$5f^{12}\ 7s^2$
Mendelevium	Md	101	$5f^{13}\ 7s^2$
Nobelium	No	102	$5f^{14}\ 7s^2$
Lawrencium	Lr	103	$5f^{14}\ 6d^1\ 7s^2$

Physical and Chemical Properties

Lanthanides are silvery white metals having low tensile strengths. They are good conductors of heat and electricity. Some of their physical properties are given below :

1. Density. Lanthanides have high densities ranging between 6.77 to 9.74 g cm^{-3}. The densities, in general, increase with increase in atomic number.

2. Melting and boiling points. Lanthanides have fairly high melting points. However, no definite trend is observed in melting and boiling points from La to Lu.

3. Ionisation energies. Lanthanides have fairly low ionisation energies. The IE_1 and IE_2 values are quite comparable to those of alkaline earth metals particularly calcium.

4. Electropositive character. Lanthanides have high electropositive character due to low ionisation energies.

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5. Coloured ions. Many of the lanthanide ions are coloured in solid state as well as in solutions. *The colour is attributed to f-f transitions since they have partly filled f-orbitals.*

6. Magnetic behaviour. The lanthanide ions (M^{3+}) generally show paramagnetism due to the unpaired electrons in *f*-orbitals.

7. Atomic/ionic radii and Lanthanide contraction. The atomic radii and ionic radii of tripositive lanthanide ions (M^{3+}) show a steady and gradual decrease in moving from La to Lu (Table 11.13). Although the atomic radii do show some irregularities but ionic radii decrease steadily from La to Lu. ***The steady decrease in the size of lanthanide ions (M^{3+}) with the increase in atomic number*** is called **lanthanide contraction.**

Cause of lanthanide contraction. As the atomic number increases in lathanide series, for every proton in the nucleus the extra electron goes to fill 4*f*-orbitals. The 4*f*-electrons constitute inner shells and are rather ineffective in screening the nuclear charge. Thus, there is a gradual increase in the effective nuclear charge experienced by the outer electrons. Consequently, the attraction of the nucleus for the electrons in the outermost shell increases as the atomic number of lanthanides increases and the electron cloud shrinks. This results in gradual decrease in size of lanthanides with increase in atomic number.

Table 11.13. Oxidation States and Atomic Radii of Lanthanides

Element	*Oxidation States*	*Atomic radius (pm)*	*Ionic Radius (M^{3+})(pm)*
La	+ 3	169	106
Ce	+ 3, + 4	165	103
Pr	+ 3, + 4	165	101
Nd	+ 2, + 3, + 4	164	100
Pm	+ 3	—	98
Sm	+ 2, + 3	166	96
Eu	+ 2, + 3	185	95
Gd	+ 3	161	94
Tb	+ 3, + 4	159	92
Dy	+ 3, + 4	159	91
Ho	+ 3	158	89
Er	+ 3	157	88
Tm	+ 2, + 3	156	87
Yb	+ 2, + 3	170	86
Lu	+ 3	156	85

Consequences of Lanthanide Contraction

Some significant consequences of lanthanide contraction are given below :

(*i*) **Similarity of second and third transition series.** The atomic radii of second row of transition elements are almost similar to those of the third row of transition elements. For example, among the elements of group 3, there is normal increase in size from Sc to Y to La. But after lanthanides the atomic radii from second to third transition series do not increase as shown below for groups 4 and 5.

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3		4	5
$_{21}Sc$ 144 pm		$_{22}T_1$ 132 pm	$_{23}V$ 122 pm
$_{39}Y$ 180 pm		$_{40}Zr$ 160 pm	$_{41}Nb$ 146 pm
$_{57}La$ 187 pm	LANTHANIDES 58—71	$_{72}Hf$ 159 pm	$_{73}Ta$ 146 pm

Here the usual increase in size on moving down the group from second to third transition elements is cancelled by the decrease in size due to lanthanide contraction. Also as a result of lanthanide contraction the second and third rows of transition elements resemble each other more closely than do the first and second row.

(*ii*) **Separation of lanthanides.** Separation of lanthanides is also possible due to lanthanide contraction. All the lanthanides have quite similar properties and due to this reason they are difficult to be separated. However, because of lanthanide contraction their properties (such as ability to form complexes) vary slightly. This slight variation in properties is utilized in the separation of lanthanides by ion exchange methods.

(*iii*) **Variation in basic strength of hydroxides.** The basic strength of hydroxides decreases from $La(OH)_3$ to $Lu(OH)_3$. *Due to lanthanide contraction size of M^{3+} ions decreases and there is increase in the covalent character in M—OH bond.*

8. Oxidation States. *The lanthanides exhibit a principal oxidation state of + 3.* The + 3 oxidation states in lanthanum, gadolinium and lutetium are especially stable because + 3 ions of these elements have an empty, a half-filled and completely filled 4*f* sub-shell respectively. Cerium and terbium also exhibit oxidation state of + 4. Ce^{4+} has configuration $4f^0$ and Tb^{4+} has the configuration $4f^7$. Sm^{2+} ($4f^6$), Eu^{2+} ($4f^7$) and Yb^{2+} ($4f^{14}$) ions also exist in aqueous solutions. Although a few lanthanides exhibit oxidation states of + 4 and + 2, yet they have the tendency to attain the oxidation state of + 3 because the + 3 oxidation state is most stable state for all lanthanides. For example, Ce^{4+} is a good *oxidising agent* while Sm^{2+} is a good *reducing agent.*

$$Ce^{4+} + Fe^{2+} \longrightarrow Ce^{3+} + Fe^{3+}$$

$$2Sm^{2+} + 2H_2O \longrightarrow 2Sm^{3+} + 2OH^- + H_2$$

In the above reactions, Ce^{4+} and Sm^{2+} are converted into + 3 ions, Ce^{3+} and Sm^{3+} respectively.

Actinides exhibit several oxidation states, however + 4 oxidation state is the most common in actinides. A few of the actinides exist in + 6 oxidation state. For example, U^{6+}, Np^{6+} and Pu^{6+}.

9. Chemical reactivity. Many lanthanides react with carbon to form salt-like carbides and with hydrogen to give salt-like hydrides. Lanthanides react with oxygen and sulphur to form oxides (M_2O_3) and sulphides (M_2S_3) respectively. Cerium gives CeO_2. The M_2O_3 oxides react with water to form insoluble hydroxides. Oxides and hydroxides on reaction with CO_2 give carbonates, $M_2(CO_3)_3$. Lanthanide compounds are generally ionic. These compounds are generally coloured and exhibit paramagnetism. These elements occur together in nature because of their great chemical similarity and are difficult to separate. However, because of lanthanide contraction they do exhibit slight variation in their properties and this becomes the basis of their separation by ion-exchange methods.

Uses of Lanthanides

The alloys of lanthanides with other metals find large number of applications in industries. Some common uses of lanthanides and their compounds are listed below :

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(*i*) ***Mischmetal, an alloy*** which contains rare earth elements (94-95%), iron (5%) and traces of sulphur, carbon, silicon, calcium and aluminium. It is *pyrophoric* and is used in cigarette and gas lighters, flame throwing tanks, tracer bullets and shells. The main rare earth elements present in this alloys are cerium (≈ 40%), lanthanum and neodymium (≈ 44%).

(*ii*) An alloy containing magnesium and about 3% mischmetal is used in jet engine parts.

(*iii*) Ceric sulphate is used as oxidising agent in volumetric analysis.

(*iv*) Cerium salts are also used in dying cotton, in lead accumulators and also as catalysts.

(*v*) Oxides of neodymium and praseodymium are used for making coloured glasses for goggles.

ACTINIDES

The series of elements involving the filling of 5*f*-orbitals is called actinide series. They follow Ac (89) and include elements from Th (90) and Lw (103).

The chemistry of **actinides** is more complicated due to the existence of greater range of oxidation states for these metals. Moreover, all these metals are radioactive and therefore, their accessibility for laboratory investigations is limited. The elements beyond uranium are all man-made elements and are made by nuclear-chemical methods. Some of the physico-chemical properties of actinides are discussed as follows.

Some Physico-chemical Properties of Actinides

1. Oxidation states. The common oxidation state of these elements is + 3. However, they also exhibit oxidation state of + 4, + 5, + 6.

2. Physical appearance. Actinides are silvery white metals. They get tarnished when exposed to the attack of alkalies.

3. Density. All the actinides except thorium and americium have high densities.

4. Colour. The actinide ions in general, are coloured. The appearance of colour depends upon the number of 5*f*-electrons. The ions containing $5f^{\circ}$ and $5f^{7}$ configurations are colourless. While those having 2 to 6 electrons in 5*f*-shell are coloured.

$$U^{3+}(5f^{3}) : Red, \quad Np^{3+}(5f^{4}) : Bluish, \quad Pu^{3+}(5f^{5}) : Blue, \quad Am^{3+}(5f^{6}) : Pink$$

5. Ionisation energies. IE values of acinides are low.

6. Electropositive character. All the known actinide metals are highly electropositive. They resemble lanthanide series in this respect.

7. Melting and boiling points. They have high melting and boiling points. They do not follow regular gradation of melting or boiling points with increase in atomic number.

8. Magnetic properties. The actinide elements are paramagnetic due to the presence of unpaired electrons.

9. Radioactive nature. All the actinides are radioactive in nature.

10. Actinide contraction. The size of atom/cation decrease regularly along the actinides series. The steady decrease in ionic radii with increase in atomic number is referred to as ***actinide contraction***. This is due to poor shielding of *5f-electrons*.

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Some significance differences between lanthanides and actinides are given below :

Lanthanides	*Actinides*
1. Besides common oxidation state of + 3, some of the lanthanides exhibit oxidation states of + 2 and + 4.	1. Besides oxidation state of + 3, they show higher oxidation state of + 4, + 5, + 6 and + 7 also.
2. They have smaller tendency of complex formation.	2. They have strong tendency of complex formation.
3. They do not form oxo ions.	3. They do form oxo ions. Some examples being UO_2^+, PuO_2^+, UO^+ etc.
4. Except promethium, they are non-radioactive.	4. All the actinides are radioactive.
5. Lanthanide compounds are less basic.	5. Actinide compounds are more basic.

Uses of Actinides

Some important uses of actinides are as follows :

1. Thorium is used in atomic reactors as fuel rods and in the treatment of cancer. A mixture of thorium and cerium nitrate in the ratio of 99 : 1 is used for making incandescent gas mentles.

2. Uranium is used as nuclear fuel. Its salts are used in glass industry (for imparting green colour), textile industry and also in medicines.

3. Plutonium is used as fuel for atomic reactors as well as in atomic bombs.

IMPORTANT TERMS AND CONCEPTS

- **Transition Elements.** Elements having incomplete *d*-orbitals in their atoms or in their simple ions.
- **Three Transition Series.** The series involving filling 3*d*, 4*d* and 5*d* sub-shell respectively.
- **Variable Oxidation States.** Transition elements exhibit variable oxidation states due to participation of $(n-1)d$-electrons in bonding.
- **Coloured Complexes.** Transition elements form coloured complexes. Colour of the complexes is due to absorption of light energy due to *d*-*d* transitions in partially filled *d*-orbitals.
- **Paramagnetic Nature.** Most of the transition element compounds are paramagnetic due to the presence of unpaired electrons in them. $\mu = \sqrt{n(n+2)}$ BM.
- **Zinc, Cadmium, Mercury** do not show characteristic properties of transition elements because they do not contain partially filled *d*-orbitals.
- **Chromate (CrO_4^{2-}) and Manganate (MnO_4^-) ions** have tetrahedral geometry.
- **Inner Transition Elements.** Elements in which last electrons enters the *f*-sub-shell of antipenultimate energy level.
- **Lanthanides.** A series of elements which involve filling of 4*f*-sub-shell. These are fourteen elements following lanthanum from Cerium to Lutetium.
- **Actinides.** A series of elements which involve filling of 5*f*-sub-shell. These are fourteen elements following Actinium from Thorium to Lawrencium.
- **Lanthanide Contraction.** The steady decrease in size of lanthanide ions (M^{3+}) with increase in atomic number.

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EXERCISE

VERY SHORT ANSWER QUESTIONS
(1 Mark)

1. Which three elements belonging to *d*-block are usually not considered as transition elements ?
2. Which transition metal has highest density ?
3. Which transition metal has highest melting point and which has lowest melting point ?
4. Why Cd^{2+} salts are white ?
5. What is the shape of chromate ion ?
6. Why tungsten is used as filament in electric bulbs ?
7. Why chromium is used for electroplating iron ?
8. Name two ores of titanium.
9. Which metals are known as ferrous metals ?
10. Out of ferrous and ferric salts which possesses higher magnetic moment ?
11. Copper (I) is diamagnetic whereas copper (II) is paramagnetic. Give reason.
12. Why $K_2Cr_2O_7$ is generally preferred to $Na_2Cr_2O_7$ in volumetric analysis although both are oxidising agent ?
13. What are transition elements ? In what way are their electronic configurations different from those of representative elements ? ***(CBSE 1993)***
14. Explain why chromium is used for coating iron.
15. Why Ti^{4+} complexes are diamagnetic ?
16. Which of the following divalent ions is likely to have maximum magnetic moment ?

$$Cr^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}$$

17. Which metal is used for galvanization of iron ?
18. What is the most characteristic oxidation state of lanthanides ? ***(A.I. CBSE 1995)***
19. Draw the structure of $Cr_2O_7^{2-}$ ion. ***(Pb. Board 1997)***
20. Which *d*-block elements are not regarded as *d*-block elements ? ***(Pb. Board 1997)***

DESCRIPTIVE QUESTIONS
(2—3 Marks)

Transition Elements

22. Why *d*-block elements are called transition elements ?
23. Why transition elements possess the following characteristics ?
    (*i*) Variable valency (*ii*) Coloured complexes (*iii*) Catalytic property.
24. Describe briefly the following physico chemical properties of transition metals
    (*i*) metallic character (*ii*) ionic radii (*iii*) complex formation.
    [A.I. CBSE (O) 1993]
25. Describe the general characteristics of manganese group.

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26. Describe the general characteristics of chromium group.
27. Give method of preparation of potassium dichromate from chromite. Give its any four uses. [A.I. CBSE (O) 1993 ; Pb. Board 1993]
28. Describe the oxidizing properties of $K_2Cr_2O_7$ taking any three examples.
29. Describe the structure of dichromate ion. Explain why all the bonds present in it are covalent.
30. Explain the following about the transition elements :
    (*i*) Magnetic behaviour (*ii*) Metallic character
    (*iii*) Oxidation states. [A.I. (O) CBSE 1991 ; H.P. Board 1993]
31. (*a*) Why do transition metals show variable oxidation states ?
    (*b*) Transition metals show paramagnetic behaviour. Why ? (CBSE 1993)
32. What are transition elements ? Discuss the magnetic behaviour shown by these elements. What is the highest oxidation state shown by any transition metal ? (CBSE 1992)
33. Give reasons :
    (*i*) K_2PtCl_6 is a well known compound whereas the corresponding Ni compound does not exit.
    (*ii*) Catalytic activity of finely divided iron in Haber's process.
    (*iii*) $[Ti(H_2O)_6]^{3+}$ is coloured while $[Sc(H_2O)_6]^{3+}$ is colourless. (CBSE 1992)
34. Give reasons :
    (*i*) First ionisation energies of 5*d* elements are higher than those of 3*d* and 4*d* elements.
    (*ii*) Transition elements show paramagnetic behaviour. [CBSE (3) 1992]
35. Give the preparation of $KMnO_4$ from pyrolusite. (PSEB 1991)
36. Describe the oxidizing properties of $KMnO_4$ taking any three examples.
37. What happens when
    (*i*) $KMnO_4$ is heated. (*ii*) $K_2Cr_2O_7$ is heated.
    (*iii*) $K_2Cr_2O_7$ is dissolved in KOH solution. (*iv*) $K_2Cr_2O_7$ reacts with acidified solution of KI.
    (*v*) SO_2 is passed through an acidic solution of potassium dichromate.
    (*vi*) $K_2Cr_2O_7$ reacts with sodium chloride in the presence of conc. H_2SO_4.
38. How is it that several transition metals act as catalysts ? Give two examples of reactions catalysed by them.
39. Why are ionization energies of 5*d* elements greater than those of 3*d*-elements ? [A.I. (O) CBSE 1991]
40. Why are Ni(II) compounds thermodynamically more stable than Pt(II) compounds while Pt(IV) compounds are relatively more stable than Ni(IV) compounds ?
41. What are the main uses of
    (*i*) Titanium metal (*ii*) Tungsten (*iii*) Vanadium ?
42. Justify that transition elements have a tendency to give coloured ions. (PSEB 1991)
43. Justify that transition elements have a tendency to show variable oxidation states. (PSEB 1991)
44. Account for the following giving reasons :
    (*i*) Zn^{2+} salts are white while Cu^{2+} salts are blue.
    (*ii*) Complexes of transition metals are generally coloured.
    (*iii*) Transition metals form large number of alloys with each other.
    (*iv*) Zn, Cd and Hg are normally not considered transition metals.
    (*v*) Transition elements have very high heats of atomisation, high densities and high melting points.
45. Discuss briefly the following physico-chemical properties of transition metals :
    (*i*) Ionisation energy (*ii*) Ionic radii (*iii*) Complex formation.
    [A.I. CBSE (O) 1992]

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46. What happens when
   (*i*) $KMnO_4$ is heated
   (*ii*) Acidified $KMnO_4$ solution is added to warm oxalic acid solution
   (*iii*) KI solution is treated with acidified $KMnO_4$ solution
   (*iv*) KI solution is treated with alkaline solution of $KMnO_4$.
47. Describe the preparation of potassium dichromate from chromite ore. ***(PSB 1995)***
48. What is chromyl chloride test ?
49. Compare the magnetic moments of the following trivalent ions.
$$Cr^{3+}, V^{3+}, Fe^{3+}$$
50. Describe the general characteristics of titanium group.
51. Copper (I) is diamagnetic whereas copper (II) is paramagnetic. Explain. ***(Haryana Board 1995)***
52. Explain how the colour of a solution of $K_2Cr_2O_7$ depends on pH of the solution. ***(A.I. CBSE 1995)***
53. Write balanced equation for the reaction of $K_2Cr_2O_7$ with ferrous sulphate in the presence of dilute H_2SO_4. ***(A.I. CBSE 1995)***
54. (*a*) Why do transition elements
   (*i*) exhibit variable oxidation states (*ii*) form coloured compounds.
   (*b*) Why does Mn(II) ion show maximum paramagnetic character among the bivalent ions of first transition series ? ***(Haryana Board 1995)***
55. Give plausible reason for the fact that the first ionization energies of transition metals are higher than those of the 3*d* and 4*d* transition metals. ***(A.I. CBSE 1995)***
56. Give plausible reason for the fact that transition metals have high enthalpy of atomization. ***(CBSE 1995)***
57. Transition elements show variable valencies. What is the reasons for it and how is this variation different from that shown by the *p*-block elements ?
58. Why do transition elements show similarities along the period as well as down the group.
59. What is the action of (*i*) heat (*ii*) dilution with alkalies on $K_2Cr_2O_7$. ***(Pb. Board 1997)***

Lanthanides and Actinides

60. What is lanthanide contraction ? Give two examples of lanthanide elements. What are the oxidation states exhibited by lanthanide elements ? ***[CBSE (1) 1992]***
61. Explain the following :
   (*i*) Why do Zr and Hf exhibit similar properties ?
   (*ii*) Why is the separation of lanthanide elements difficult ? ***(CBSE 1991)***
62. Why are the atomic radii of the second and third series of transition elements almost equal ?
63. What is lanthanide contraction ? What are the consequences to lanthanide contraction ? ***(PSEB 1991)***
64. What are the oxidation states exhibited by lanthanide elements ?
65. What are actinides ? Give two examples of actinides. Mention with balanced equation, one oxidising reaction of potassium dichromate in acidic media. ***[CBSE (3) 1992]***
66. Give any four uses of lanthanides.
67. What is lanthanide contraction ? How does it affect the physical and chemical properties of the elements of lanthanide series ? ***(CBSE 1997)***
68. What is the general configuration of actinides ? ***(Pb. Board 1997)***
69. Which out of Sc^{3+} and Cr^{3+} exhibit paramagnetism and why ? ***(CBSE 1997)***
70. Which out of V or Mn exhibit more number of oxidation states ? ***(CBSE 1997)***

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select the correct answer from each of the following questions :

1. The general outer electronic configuration of transition element is
   (*a*) $(n-1)\,d^{1-10}\,ns^1$ (*b*) $(n-1)\,d^{10}\,ns^2$ (*c*) $(n-1)\,d^{1-10}\,ns^{1-2}$ (*d*) $(n-1)\,d^5\,ns^1$.
2. Which one of the following does not show different oxidation states ?
   (*a*) Iron (*b*) Copper (*c*) Zinc (*d*) Manganese.
3. Which of the following is not a condition for complex salt formation ?
   (*a*) Small size (*b*) Higher nuclear charge
   (*c*) Availability of vacant *d*-orbitals (*d*) Variable oxidation states.
4. Which of the following metals is used in incandescent lamps ?
   (*a*) Chromium (*b*) Tungsten (*c*) Zirconium (*d*) Molybdenum.
5. The electronic configuration of chromium is
   (*a*) $4s^1\,3d^5$ (*b*) $4s^2\,3d^4$ (*c*) $4s^0\,3d^6$ (*d*) $4s^2\,3d^5$.
6. Which ion gives coloured solution ?
   (*a*) Cu^+ (*b*) Zn^{2+} (*c*) Ag^+ (*d*) Fe^{2+}.
7. Paramagnetism is a property of
   (*a*) completely filled electronic sub-shells (*b*) unpaired electrons
   (*c*) non-transition elements (*d*) m. pt. and b. pt. of elements.
8. Which one of the following metals is used as a catalyst is the Haber's process ?
   (*a*) Tungsten (*b*) Molybdenum (*c*) Chromium (*d*) Iron containing Mo.
9. When manganese dioxide is fused with KOH in air, it gives
   (*a*) potassium permanganate (*b*) potassium manganate
   (*c*) manganese hydroxide (*d*) Mn_3O_4.
10. Which metal has highest melting point ?
    (*a*) Pt (*b*) W (*c*) Pd (*d*) Au.
11. Which metal has lowest melting point ?
    (*a*) Cs (*b*) Na (*c*) Hg (*d*) Sn.
12. Which is the first man-made element ?
    (*a*) Sc (*b*) Os (*c*) Tc (*d*) Zr.
13. Which metal has highest density ?
    (*a*) Pt (*b*) Hg (*c*) Pd (*d*) Os.
14. Which transition metal has highest density ?
    (*a*) Os (*b*) Zn (*c*) Sc (*d*) La.
15. Which transition metal can show highest oxidation state ?
    (*a*) Sc (*b*) Ti (*c*) Os (*d*) Zn.
16. In $KMnO_4$ oxidation number of Mn is
    (*a*) + 2 (*b*) + 4 (*c*) + 6 (*d*) + 7.

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17. When $KMnO_4$ acts as oxidising agent in alkaline medium, the oxidation number of Mn decreases by
(a) 1 (b) 2 (c) 3 (d) 5.

18. Ag^+ ion is isoelectronic with
(a) Cu^+ (b) Cd^{2+} (c) Zn^{2+} (d) Pd^{2+}

19. The transition element with lowest atomic number is
(a) Scandium (b) Titanium (c) Zinc (d) Lanthanum.

20. Which of the following oxides is amphoteric in nature ?
(a) NiO (b) ZnO (c) CoO (d) FeO.

21. Which of the following oxides is acidic in nature ?
(a) CrO (b) Cr_2O_3 (c) CrO_3 (d) CrO_2.

22. The equivalent mass of $K_2Cr_2O_7$, when it acts as oxidising agent in acidic medium, is equal to
(a) M (b) M/2 (c) M/6 (d) M/5.

23. Rutile is an ore of
(a) Scandium (b) Titanium (c) Manganese (d) Chromium.

24. If two compounds have the same crystal structure and analogous formula, they are called
(a) Isomers (b) Isotopes (c) Isobars (d) Isomorphous.

25. Which of the following would be diamagnetic ?
(a) Cu^{2+} (b) Ni^{2+} (c) Cd^{2+} (d) Ti^{3+}.

26. Which of the following would be paramagnetic ?
(a) Zn^{2+} (b) Cu^+ (c) Sc^{3+} (d) Mn^{2+}.

27. Which of the following is likely to form white salts ?
(a) Cu^{2+} (b) Sc^{3+} (c) Ti^{3+} (d) Fe^{3+}.

28. Which of the following has the maximum number of unpaired electrons ?
(a) Fe^{2+} (b) Cr^{3+} (c) Fe^{3+} (d) Co^{2+}.

29. In the first transition series, the element with highest melting point is
(a) Mn (b) Fe (c) Cr (d) Cu.

30. The most common oxidation state of lanthanides is
(a) + 4 (b) + 3 (c) + 6 (d) + 2.

31. Which element among the lanthanides has the smallest atomic radius ?
(a) Cerium (b) Lutetium (c) Europium (d) Gadolinium.

32. Which of the following oxides of chromium is amphoteric in nature ?
(a) CrO (b) Cr_2O_3 (c) CrO_3 (d) CrO_5.

33. Which compound of chromium is widely used in tanning of leather ?
(a) $CrCl_3$ (b) Cr_2O_3 (c) CrO_2Cl_2 (d) $K_2SO_4.Cr_2(SO_4)_3.24H_2O$.

34. Which of the following elements belongs to actinide series ?
(a) La (b) Gd (c) Lu (d) Th.

35. Ammonium dichromate is used in some fireworks. The green coloured powder blown in air is
(a) CrO_3 (b) Cr_2O_3 (c) Cr (d) $CrO(O_2)$. *(I.I.T. 1997)*

36. The number of moles of $KMnO_4$ that will be needed to react with one mole of sulphite ion in acidic solution is
(a) 2/5 (b) 3/5 (c) 4/5 (d) 1 *(I.I.T. 1997)*

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37. Which of the following compound is expected to coloured
(a) Ag_2SO_4 (b) CuF_2
(c) MgF_2 (d) CuCl. *(I.I.T. 1997)*

38. CrO_3 dissolves in aqueous NaOH to give
(a) CrO_4^{2-} (b) $Cr(OH)_3$
(c) $Cr_2O_7^{2-}$ (d) $Cr(OH)_2$. *(CBSE Ent. 1997)*

FILL IN THE BLANKS

1. The most abundant transition metal is ..... .
2. Ilmenite is an ore of ..... .
3. In acidic medium $KMnO_4$ is reduced to ..... .
4. The formula of pyrolusite is ..... .
5. Among transition element, the element having lowest m. pt. is ..... .
6. The common oxidation state of lanthanides is ..... .
7. The common oxidation state of actinides is ..... .
8. The ferrous metals are ..... .
9. The last element of lanthanide series is ..... .
10. Ce (IV) salts are good ..... agents.
11. The acidic oxide of manganese is ..... .
12. CrO_4^{2-} ion has ..... geometry.
13. The metal having highest melting point is ..... .
14. *f*-Block elements are also known as ..... .
15. Lanthanides have ..... densities.

TRUE/FALSE STATEMENTS

1. Lanthanides form coloured complexes.
2. Lanthanides are generally diamagnetic.
3. Iron, cobalt and nickel are ferromagnetic.
4. Principal oxidation state of lanthanides is + 3.
5. Zinc salts are generally coloured.
6. Ag (I) salts are diamagnetic.
7. An aqueous solution of K_2MnO_4 is violet in colour.
8. In $CuCl_2$ coordination number of copper is six.
9. Principal oxidation state of actinides is + 4.
10. Transition elements exhibit variable oxidation states.

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HINTS/ANSWERS

REVIEW PROBLEMS

11.1. Yttrium and Cadmium **11.2.** Zn, Cd, Hg **11.3.** Sc—lightest ; Os—heaviest

11.4. $(n-1)\,d^{1-10}\,ns^{1-2}$ **11.5.** (*i*) Hg (*ii*) W **11.8.** Zn^{2+}, Ti^{4+}, Cd^{2+}

11.10. *Acidic* : Mn_2O_7, CrO_3, V_2O_5 ; *Basic* : MnO, VO, Cu_2O

11.11. Due to oxidation of H_2S to colloidal S **11.13.** CrO_2Cl_2

11.17. + 2 **11.19.** Fe, CO, Ni

VERY SHORT ANSWER QUESTIONS

1. Zn, Cd, Hg
2. Osmium
3. Highest m.p.—Tungsten ; Lowest m.p.—Mercury
4. They have fully-filled *d*-orbitals, hence, *d*-*d* transitions are not possible.
5. Tetrahedral
6. Due to high m.p. and high resistance
7. Due to formation of inert layer of oxide.
8. Rutile (TiO_2) and ilmenite ($FeTiO_3$)
9. Iron, cobalt and nickel.
10. Ferric, because it has more number of unpaired electrons.
11. $K_2Cr_2O_7$ is not hygroscopic like $Na_2Cr_2O_7$ and it also fulfills the requirements of primary standard.
14. Because it is rendered passive due to formation of a protective layer of its oxide on the surface.
15. It has no unpaired electrons Ti^{4+} : $1s^2, 2s^2, 2p^6, 3s^2\,3p^6$.
17. (*a*) Zinc
18. + 3
20. Zn, Hg, Cd.

MULTIPLE CHOICE QUESTIONS

1. (*c*)	2. (*c*)	3. (*d*)	4. (*b*)	5. (*a*)	6. (*d*)
7. (*b*)	8. (*d*)	9. (*b*)	10. (*b*)	11. (*c*)	12. (*c*)
13. (*d*)	14. (*a*)	15. (*c*)	16. (*d*)	17. (*c*)	18. (*b*)
19. (*a*)	20. (*b*)	21. (*c*)	22. (*c*)	23. (*b*)	24. (*d*)
25. (*c*)	26. (*d*)	27. (*b*)	28. (*c*)	29. (*c*)	30. (*b*)
31. (*b*)	32. (*b*)	33. (*d*)	34. (*d*)	35. (*b*)	36. (*a*)
37. (*b*)	38. (*a*)				

FILL IN THE BLANKS

1. Iron	2. Titanium	3. Mn^{2+}
4. MnO_2	5. Mercury	6. + 3
7. + 4	8. Fe, Co, Ni	9. Lutetium
10. Oxidising	11. Mn_2O_7	12. tetrahedral
13. Tungsten	14. Inner transition elements	15. high

TRUE/FALSE STATEMENTS

1. True	2. False	3. True	4. True	5. False	6. True
7. False	8. True	9. True	10. True		

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12

Co-ordination Compounds and Organometallics

LEARNING OBJECTIVES

In this unit, we shall learn

- *Co-ordination compounds, Nomenclature ;*
- *Isomerism and applications of co-ordination compounds*
- *Compounds containing metal-carbon bond*
- *Application of organometallics*

It is a matter of common observation, that when two or more stable compounds are allowed to combine together in stoichiometric proportions these result in the formation of crystalline substances called molecular or addition compounds. A few examples are given below :

(*i*) $KCl + MgCl_2 + 6H_2O \longrightarrow KCl.MgCl_2.6H_2O$
(Carnallite)

(*ii*) $K_2SO_4 + Al_2(SO_4)_3 + 24H_2O \longrightarrow K_2SO_4.Al_2(SO_4)_3.24H_2O$
(Potash alum)

(*iii*) $(NH_4)_2SO_4 + FeSO_4 + 6H_2O \longrightarrow FeSO_4.(NH_4)_2SO_4.6H_2O$
(Mohr's salt)

(*iv*) $CuSO_4 + 4NH_3 \longrightarrow CuSO_4.4NH_3$
(Tetraammine copper sulphate)

(*v*) $Fe(CN)_2 + 4KCN \longrightarrow Fe(CN)_2.4KCN$
(Pot. ferrocyanide)

These addition compounds fall into two categories, namely ; *double salts and co-ordination compounds.*

(*a*) **Double salts.** These are the addition compounds which are stable in the solid state but break up into its constituents in dissolved state. In such compounds the individual properties of the constituents are not lost. For example, an aqueous solution of carnallite ($KCl.MgCl_2.6H_2O$) shows the properties of K^+, Mg^{+2} and Cl^- ions.

(*b*) **Co-ordination compounds.** These are the addition compounds which retain their identity in the solid as well as in the dissolved state. In such compounds the individual properties of the constituents are usually lost. For example, when we mix aqueous solution of copper sulphate with aqueous solution of ammonia, a deep blue coloured solution is formed. The blue coloured solution does not show the presence of Cu^{2+} but instead it contains cupro-ammonium ions ; $[Cu(NH_3)_4]^{2+}$ which are formed by combination of Cu^{2+} ion and four ammonia molecules. Such ions are known as **complex ions.** Similarly, a complex ion ferrocyanide $[Fe(CN)_4]^{4-}$ is formed on mixing aqueous solutions of KCN and $Fe(CN)_2$ in definite proportions. The salts of the complex ions are called **complex compounds** or **co-ordinate compounds.**

The term co-ordination is coined for such addition compounds because in all such compounds the central metal ion forms dative or co-ordinate bonds with species surrounding it.

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The branch of inorganic chemistry that deals with the study of co-ordination compounds is known as co-ordination chemistry.

In this unit, we shall study the basic guiding principles of the chemistry of co-ordination compounds, the nature of these compounds with special reference to bonding in these compounds and uses and industrial applications of these compounds. Apart from these, we shall also briefly study the chemistry of organometallic compounds which contain metal-carbon bonds. Before we go into the finer details of the various aspects of co-ordination compounds let us briefly discuss a few terms that we shall be using in the text.

12.1. TERMINOLOGY

Co-ordination Compound

A co-ordination compound contains a central metal atom or cation which is surrounded by a suitable number of anions or neutral molecules and usually retains its identity in solutions as well as in solid state. To add a point further, in these compounds, the number of species surrounding the central metal atom is beyond its electrovalency or covalency. For example, in $[Cu(NH_3)_4]SO_4$, the electrovalency of copper is two, but it is surrounded by four NH_3 molecules. These ions or molecules (co-ordinated group or donor) attached to the central metal ion are called *ligands.*

A co-ordination compound generally contains one or more complex ions. For example,

$[Cu(NH_3)_4]SO_4$	contains	$[Cu(NH_3)_4]^{2+}$	complex ion
$Na[Ag(CN)_2]$	contains	$[Ag(CN)_2]^-$	complex ion
$[Ag(NH_3)_2]Cl$	contains	$[Ag(NH_3)_2]^+$	complex ion.
$[Cr(CN)_6][Co(NH_3)_6]$	contains	$[Cr(CN)_6]^{3-}$	and $[Co(NH_3)_6]^{3+}$ complex ion

Complex ion

A complex ion is an electrically charged radical or species, carrying positive or negative charge, in which the central atom or ion is surrounded by a suitable number of neutral molecules or negative ions (called ligands). Some common examples are :

$$[Ni(NH_3)_6]^{2+}, [Co(NH_3)_4]^{2+}, [PtCl_6]^{2-}, [Ag(CN)_2]^-,$$
$$[Fe(CN)_6]^{4+}, [Fe(C_2O_4)_3]^{3-}, [Ni(CO)_4], [Co(NH_3)_4Cl_2]$$

The complex ion carrying a positive charge is called *cationic complex,* the one with a negative charge is called *anionic complex* and the one with no charge is called a *neutral complex.*

Ligand

The neutral molecules or ions that surround the metal ion in a complex are known as ligands (derived from the Latin word *ligare* meaning *to bind*). Ligands are normally polar molecules such as $\ddot{N}H_3$, $H_2\ddot{O}$: or anions such as Cl^-, OH^-, CN^-, etc., which have at least one unshared pair of valence electrons. They get attached to the central metal ion by a *co-ordinate or dative bond.* The atom in the ligand which is involved in the formation of co-ordinate bond with central metal atom is called **co-ordinating atom** or **donor atom.** A donor atom is also referred to as *donor site* of the ligand. A ligand may contain one or more donor sites. Depending upon the number of donor sites, the ligands may be classified as :

unidentate (one donor site)

bidentate (two donor sites)

tridentate (three donor sites)

tetradentate (four donor sites)

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hexadentate (six donor sites), etc.

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Ligands with more than one donor sites are collectively called **multidentate ligands.**

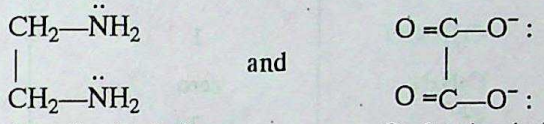
It may be noted that an atom can have only one donor site but a molecule can have more than one donor sites.

Some of the common examples of the monodentate ligands are given in Table 12.1 given below.

Chelating ligands

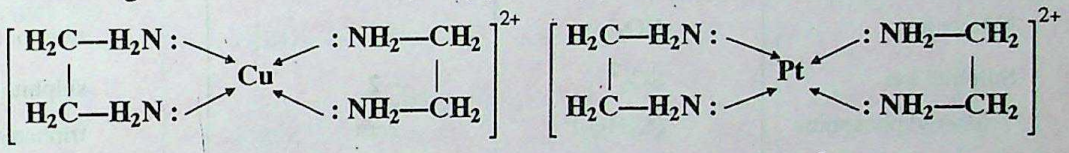
When a multidentate ligand simultaneously co-ordinates to a metal ion by more than one donor site, then a ring-like structure is obtained. It is called a *chelate ring* and the ligand is known as **chelating ligand** (from Greek word *chele* meaning *claw*).

Some common examples of bidentate ligands are :



Ethylene diamine (*en*) and Oxalate ion (*ox*)

The chelate ring like structures formed by Cu(II) and Pt(II) with ethylene diamine are shown below :



$[Cu(en)_2]^{2+}$ *ion* $[Pt(en)_2]^{2+}$

Some examples of chelating ligands are given in Table 12.2.

Some noteworthy points about the chelates :

(*i*) Chelating ligands form more stable complexes than the monodentate ligands. For example,

$$[Co(H_2O)_6]^{2+} + 3en \longrightarrow [Co(en)_3]^{2+} + 6NH_3$$

The complex of ethylenediammine with cobalt is more stable than the complex with water. *This is because when chelation occurs entropy increases and the process becomes more favourable.*

(*ii*) Ligands with larger groups form unstable rings than the ligands with smaller groups. *This is ascribable to steric hinderance produced by a larger group.*

Table 12.1. Some Common Unidentate Ligands

Name	*Formula*	*Charge*	*Name of ligand*
Ammonia	$\ddot{N}H_3$	zero	ammine
Water	$H_2\ddot{O}$:	zero	aquo or aqua
Halide ion	X^- (X = Cl, Br, I)	– 1	halo
Hydroxide ion	$: OH^-$	– 1	hydroxo
Cyanide ion	$: CN^-$	– 1	cyano
Oxide ion	O^{2-}	– 2	oxo
Peroxide ion	O_2^{2-}	– 2	peroxo
Carbonate ion	CO_3^{2-}	– 2	carbonato

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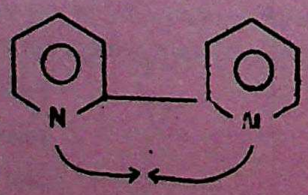
Name	*Formula*	*Charge*	*Name of ligand*
Phosphine	$\ddot{P}H_3$	zero	phosphine
Nitrogen oxide	NO	zero	nitrosyl
Carbon monoxide	CO	zero	carbonyl
Sulphate ion	SO_4^{2-}	– 2	sulphato
Nitrite ion	NO_2^-	– 1	nitro or nitrito*
Thiocyanate ion	SCN^-	– 1	thiocyanato or isothiocyanato*
Acetate ion	CH_3COO^-	– 1	acetato
Pyridine	$C_5H_5\ddot{N}$	zero	pyridine (py)
Sulphide ion	S^{2-}	– 2	sulphido
Thiosulphate	$S_2O_3^{2-}$	– 2	thiosulphato
Nitrate ion	NO_3^-	– 1	nitrato
Sulphite ion	SO_3^{2-}	– 2	sulphito
Triphenyl phosphine	$(C_6H_5)_3\ddot{P}$	zero	triphenyl phosphine
Thiocarbonyl	CS	zero	thiocarbonyl
Nitrosonium	NO^+	+ 1	nitrosonium
Nitronium	NO_2^+	+ 1	nitronium
Imide ion	NH^{2-}	– 2	imido
Nitrate ion	NO_3^-	– 1	nitrato
Amide ion	NH_2^-	– 1	amido
Thio urea	H_2NCSNH_2	zero	thiourea (tu)

*See section 12.5—Linkage isomerism.

Table 12.2. Some Multidentate Ligands

Name of the species	*Formula*	*Charge*	*Abbreviation*	*Donor sites*
Ethylenediamine	$\ddot{N}H_2CH_2CH_2\ddot{N}H_2$	zero	en	2
2, 2′-Bipyridyl		zero	bipy	2

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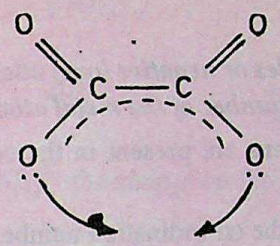
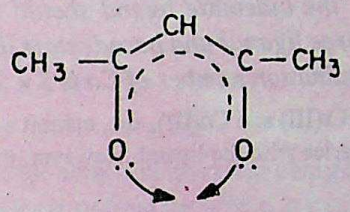
Name of the species	*Formula*	*Charge*	*Abbreviation*	*Donor sites*
Oxalate ion		– 2	ox	2
Acetylacetonate		– 1	acac	2
Dimethylglyoxime ion	$CH_3C{=}NO^-$ | $CH_3C{=}\ddot{N}{-}OH$	– 1	dmg	2
Diethylene triamine	H_2C < $CH_2\ddot{N}H_2$, $\ddot{N}H$; H_2C < $\ddot{N}H$, $CH_2\ddot{N}H_2$	zero	dien	3
Triethylene tetraamine	$CH_2\ddot{N}H(CH_2)_2NH_2$ | $CH_2\ddot{N}H(CH_2)_2\ddot{N}H_2$	zero	trien	4
Ethylenediamine triacetate ion	$CH_2{-}N$ < CH_2COO^-, CH_2COO^- ; | $CH_2{-}N$ < H, CH_2COO^-	– 3	$EDTA^{3-}$	5
Ethylenediamine tetra-acetate ion	$CH_2{-}\ddot{N}$ < CH_2COO^-, CH_2COO^- ; | $CH_2{-}\ddot{N}$ < CH_2COO^-, CH_2COO^-	– 4	$EDTA^{4-}$	6

Co-ordination sphere

In the complexes, the central metal ion alongwith the non-ionisable ligands attached to it is always written in a square bracket [ ]. This part of the complex is called *co-ordination sphere*. The portion present outside the square brackets is called *ionisation sphere*. For example, in a complex $[Cu(NH_3)_4]SO_4$, the part $[Cu(NH_3)_4]^{2+}$ is called co-ordination sphere and SO_4^{2-} constitutes ionisation spheres. It may be noted that :

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(*i*) ***species present in the co-ordination sphere are non ionisable.***

(*ii*) ***species present in the ionisation sphere are ionisable.***

Co-ordination number

The total number of ligands (neutral molecules or negative ions) attached to the central metal atom in the co-ordination sphere is called co-ordination number of the metal atom. *For example,*

(*i*) In the complex $K_2[PtCl_6]$, six chloride ions are present in the co-ordination sphere, therefore, co-ordination number of Pt is **6**.

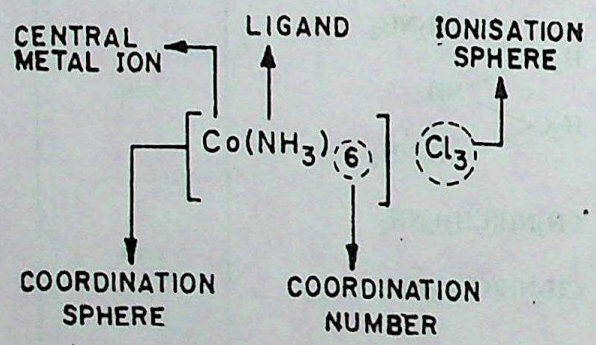
(*ii*) Similarly, in the complex $[Ni(NH_3)_4]Cl_2$, the co-ordination number of Ni is **4**.

For calculating the co-ordination number the bidentate ligand should be counted as two ligands. Similarly, tridentate ligand should be counted as three ligands and hexadentate ligand shouled be counted as six ligands. For example, in $[Co(en)_3]^{3+}$, the co-ordination number of Co is $3 \times 2 = 6$.

It must be noted here that only some metals like Cr(III) and Co(III), etc., exhibit a constant co-ordination number whereas in most of the ions the co-ordination number varies with the ligand. However, the most common co-ordination numbers are four and six.

In the formation of a complex of $CoCl_3$ with NH_3, the complex compound is suitably labelled to clearly illustrate the various terms as discussed above.

$$CoCl_3 + 6NH_3 \longrightarrow CoCl_3 \,.\, 6NH_3.$$



Oxidation number or oxidation state or charge on central metal ion

The oxidation number is the residual charge that appears on the central atom when all other atoms/ions are removed from it. Similarly, the charge on a complex is the sum of the charges of the constituent parts *i.e.*, the sum of the charges on the central metal ion and its surrounding ligands. It must be noted that :

(*i*) the sum of charges of the constituents is equal to zero if the complex is neutral and

(*ii*) for an anionic or cationic complex, the sum of charges of the constituents is equal to the charge on the co-ordination sphere.

The above points are illustrated by taking the following examples.

(*i*) In the complex $[Co(en)_2Cl(ONO)]$ the charge on the complex is zero, whereas the charge on the central metal ion may be calculated as under :

$$\begin{array}{cccccc} [Co & & (en)_2 & & Cl & (ONO)] \\ \downarrow & & \downarrow & & \downarrow & \downarrow \\ x & + & 2(0) & + & (-1) & +(-1) = 0 \end{array}$$

$$x = +2$$

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(*ii*) Similarly, in the complex ion $[Co(NH_3)_2Cl_4]^{2+}$ the charge on the cationic complex is + 2 and the charge on the central metal ion is

$$[Co \qquad (NH_3)_2 \qquad Cl_4]^{2-}$$
$$\downarrow \qquad \downarrow \qquad \downarrow$$
$$x + \qquad 2(0) \qquad + 4(-1) = -2$$
$$x = +2$$

(*iii*) In the complex, $[Fe(CN)_6]^{4-}$ the charge on the complex ion is – 4 and the oxidation number of central metal is

$$[Fe \qquad (CN)_6]^{4-}$$
$$\downarrow$$
$$x + 6(-1) = -4$$
$$x = +2$$

It must be noted here that the total electrovalent charge on the complex ion changes with the number of charged ion which may enter into co-ordination sphere to replace neutral molecules. The ammine complexes of platinum (IV) illustrate these variable combinations as shown in Table 12.3.

Table 12.3. Ammine Complexes of Platinum (IV)

Formula	*Co-ordination sphere*	*Ionisation sphere*	*Total no. of ions in aq. sol.*
$[Pt(NH_3)_6]Cl_4$	$[Pt(NH_3)_6]^{4+}$	$4Cl^-$	5
$[Pt(NH_3)_5Cl]Cl_3$	$[Pt(NH_3)_5Cl]^{3+}$	$3Cl^-$	4
$[Pt(NH_3)_4Cl_2]Cl_2$	$[Pt(NH_3)_4Cl_2]^{2+}$	$2Cl^-$	3
$[Pt(NH_3)_3Cl_3]Cl$	$[Pt(NH_3)_3Cl_3]^{+}$	Cl^-	2
$[Pt(NH_3)_2Cl_4]$	$[Pt(NH_3)_2Cl_4]$	—	0
$K[Pt(NH_3)Cl_5]$	$[Pt(NH_3)Cl_5]^-$	K^+	2
$K_2[PtCl_6]$	$[PtCl_6]^{2-}$	$2K^+$	3

Effective Atomic Number (EAN)

EAN of the central metal atom/ion in a complex can be calculated by using the following formula. If Z is the atomic number of the central metal atom/ion, (*ON*) is its oxidation number and (*CN*) is its co-ordination number. Then $EAN = Z - ON + 2(CN)$.

REVIEW QUESTIONS

12.1. What is the oxidation number of central atom is each of the following ?

(*i*) $[Pt(NH_3)_6]Cl_4$ (*ii*) $Fe_4[Fe(CN)_6]_3$
(*iii*) $Ni(CO)_4$ (*iv*) $Na[Hg(CN)_2]$.

12.2. What is the co-ordination number of central metal atom in the following ?

(*i*) $[Pt(NH_3)_3Cl_3]Cl$ (*ii*) $K_3[Fe(C_2O_4)_3]$
(*iii*) $[Fe(EDTA)]^-$ (*iv*) $[Rh\{P(C_6H_5)_3\}_3]Cl$.

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12.3. How many moles of Cl^- ions are furnished by one mole of each of the following ?

(*i*) $[M(NH_3)_4Cl_2]Cl_2$ (*ii*) $K_2[PtCl_6]$

(*iii*) $[Pt(NH_3)_3Cl_3]Cl$ (*iv*) $[Cr(NH)_3]Cl_3$.

12.4. Which of the following will give white precipitate with $AgNO_3$ solution ?

(*i*) $[Co(Py)_2(H_2O)_2Cl_2]Cl$ (*ii*) $[Co(Py_2)H_2OCl_3]H_2O$.

12.5. What is the EAN of central metal atom in each of the following complexes ?

(*i*) $K_4[Fe(CN)_6]$ (*ii*) $K_3[Fe(CN)_6]$

(*iii*) $[Ni(NH_3)_6]Cl_2$ (*iii*) $[Cu(CN)_4]^{3-}$

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12.2. WERNER'S THEORY

The early study of inorganic complex compounds merely dealt with the attempts to explain the existence and structure of hydrated double salts like Mohr's salt, carnallite, etc. Though, the early theories developed during the era could provide a satisfactory explanation of the formation and properties of mixed salts yet these offered no adequate explanation of the union of neutral molecules with ions to form complex compounds as listed in Table 12.4. The chemists wondered about how the atoms in these complexes were connected to each other and the possible effect of the arrangement on the properties of the complexes.

Table 12.4

Formula	*Colour*	*Historical name*	*Modern formulation*
$CoCl_3.6NH_3$	orange	luteo cobaltic chloride	$[Co(NH_3)_6]Cl_2$
$CoCl_3.5NH_3.H_2O$	rose	roseo cobaltic chloride	$[Co(NH_3)_5H_2O]Cl_3$
$CoCl_3.5NH_3$	purple	purpureo cobaltic chloride	$[Co(NH_3)_5Cl]Cl_2$
$CoCl_3.4NH_3$	green	praseo cobaltic chloride	trans-$[Co(NH_3)_4Cl_2]Cl$
$CoCl_3.4NH_3$	violet	violeo cobaltic chloride	cis-$[Co[NH_3]_4Cl_2]Cl$
$CoCl_3.3NH_2$	blue-green	—	$[Co(NH_3)_3Cl_3]$

The first successful theory explaining the properties of co-ordination compounds in terms of their structure was proposed by Alfred Werner around 1893, long before sophisticated techniques were developed and the concepts of electronic structure were applied to chemical system. **The brief outlines of his theory are :**

(*i*) *Metals have two types of linkages (valencies) i.e.,* **primary** and **secondary linkages.** *The primary linkages are satisfied by the negative ions whereas the secondary linkages may be satisfied either by the negative ions or by neutral molecules. The primary valencies are ionisable valencies whereas the secondary valencies are non-ionisable valencies.*

According to the modern concept the primary valencies usually indicate the oxidation number of the metal ion whereas the secondary valencies refer to the co-ordination number.

For example, in the compound $CoCl_3$, the primary valency of Co is 3. When addition of ammonia is done to $CoCl_3$, it yields a complex compound $CoCl_3.6NH_3$. In this case the primary valencies are satisfied by three chloride ions whereas the secondary valencies are satisfied by ammonia molecules. *Thus, every metal atom has a tendency to satisfy both its primary as well as secondary valencies.*

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(*ii*) *Each metal atom can have a characteristic number of secondary valencies about the central atom. These valencies are projected in the space about the central atom in such a manner that these assign a definite geometry to the co-ordination compound.*

For example, in $CoCl_3.6NH_3$, the six secondary valencies are arranged in an **octahedral fashion** around the central metal ion. On the other hand, if there are four secondary valencies as in the case of $CoCl_3.4NH_3$ then these shall have either a **tetrahedral** or **a square planar** arrangement.

(*iii*) *Not only the neutral molecules be co-ordinated to the central atom but ions may also be co-ordinated in same fashion. When an ion replaces a neutral molecule in the coordination sphere, it loses its electrovalent character and gets attached to the central ion by non-ionisable linkage.*

For example, the co-ordination compounds $[Co(NH_3)_5Br]^{2+}SO_4^{2-}$ and $[Co(NH_3)_5SO_4]^{+}Br^{-}$ have the same formula. In the former, as the SO_4^{2-} ion is present outside the co-ordination sphere it gives a white precipitate with $BaCl_2$. When this ion replaces the Br^- ion (in the latter) in the co-ordination sphere it loses it ionic character *i.e.*, no precipitates are obtained with $BaCl_2$.

The above point is also illustrated in formation of complex of Pt^{4+} ion with ammonia and Cl^- ion as shown in Table 12.3.

Assignment of Structure on the Basis of Werner's Theory

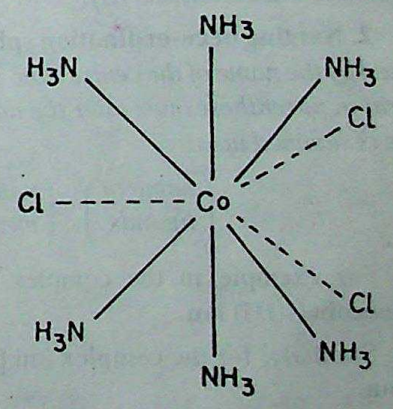
Werner, on the basis of his auxiliary valence theory, assigned structural formula to a number of co-ordination compounds. For instance, cobaltic chloride combines with NH_3 in different stoichiometric ratios to yield a number of compounds at listed in Table 12.4. In all the compounds the co-ordination number of cobalt is six but these differ from each other in respect of the ions or neutral molecules present in the co-ordination sphere.

Structure of $CoCl_3.6NH_3$

(*i*) The complex is found to give white precipitate with $AgNO_3$ indicating the presence of ionisable chlorine atom(s). Quantitative analysis reveals that AgCl precipitates corresponding three chloride ions are obtained indicating the presence of three ionisable chlorine atoms. *Thus, chlorine atoms are bonded to cobalt by three primary valencies.*

(*ii*) The solution of the complex does not give test for Co^{2+} ions indicating that cobalt and NH_3 molecules constitute the co-ordination sphere, where as the *neutral ammonia molecules satisfy the secondary valencies.*

(*iii*) As six neutral ligands surround the central ion, therefore to have minimum electronic repulsions these project towards the six ends of a octahedron giving rise to *octahedral geometry.*



Thus, the complex may be formulated as $[Co(NH_3)_6]Cl_3$ and is pictorially represented above.

For the sake of distinction the primary valencies are shown in dotted lines whereas the secondary valencies are in bold lines.

On the basis of similar discussion, the structure of other cobalt complexes with ammonia are as follows :

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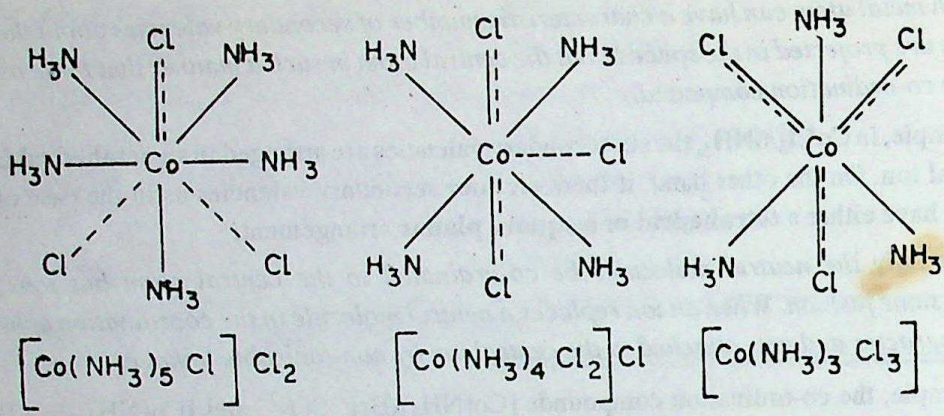

Chlorine atom with bold and dotted line indicates that it satisfies both the primary as well as secondary valency.

12.3. NOMENCLATURE OF CO-ORDINATION COMPOUNDS

As the co-ordination compounds (or complexes) can be sufficiently complicated, a few formal rules were suggested by the IUPAC to name these compounds. These rules are as stated below :

1. Order of naming ions. *If the compound is ionic, the name of cation is mentioned first followed by the name of anion.* For example,

In the complex $K_2[PtCl_6]$, *the name of cation, potassium is written first followed by the name of anion* $[PtCl_6]^{2-}$ *i.e., hexachloroplatinate (IV).*

Similarly, in the complex $[Co(NH_3)_5Cl]Cl_2$, the name of complex part, $[Co(NH_3)_5Cl]^{2+}$ penta-ammine-chlorocobalt (III) is written first followed by name of anion, Cl^- *i.e.,* chloride.

For the *non-ionic complexes like* $[Ni(NH_3)_4Cl_2]$ *the name of complex is written in one word i.e., tetraammine dichloronickel (II).*

2. Naming of co-ordination sphere. *In naming the complex, the names of the ligands are written first followed by the name of the central ion. The oxidation number of the central metal atom is expressed by Roman numeral in parentheses just after the name of the central metal atom. The sequence of naming co-ordination sphere is summed up as :*

$$\begin{pmatrix}\textit{name of}\\ \textit{ligands}\end{pmatrix}\begin{pmatrix}\textit{name of central}\\ \textit{metal atom}\end{pmatrix}\begin{pmatrix}\textit{oxidation number of metal}\\ \textit{in Roman numeral}\end{pmatrix}$$

For example in the complex ion, $[Co(NH_3)_6]^{3+}$, the co-ordination sphere is named as **Hexa-amminecobalt(III) ion.**

Similarly, for the complex ion $[Fe(CN)_6]^{3-}$, the coordination sphere is named as **Hexacyanoferrate (III) ion.**

3. Naming of ligands. The central metal ion in a complex is surrounded by positive or negative or neutral ligands.

(*a*) *For the ligands carrying a negative charge the name has a characteristic ending word "O".* A few example are quoted below :

CH_3COO^- *Acetato*	NCS^- *Isothiocyanato*	N^{3-} *Nitrido*
NH_2^- *Amido*	NO_2^- *Nitro*	S^{2-} *Sulphido*
Cl^- *Chloro*	O^{2-} *Oxo*	

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CN^- *Cyano* O_2^{2-} *Peroxo*

CO_3^{2-} *Carbonato* $C_2O_4^{2-}$ *Oxalato*

OH^- *Hydroxo* SO_4^{2-} *Sulphato*

NH^{2-} *Imido* SCN^- *Thiocyanato*

(*b*) *For the ligands carrying a positive charge, the name of the ligand has a characteristic ending of* "**ium**". For example,

NO_2^+ *Nitronium* $[NH_2NH_3]^+$ *Hydrazinium*

NO^+ *Nitrosonium.*

(*c*) *For neutral ligands no characteristic ending is used.* For example,

$NH_2CH_2CH_2NH_2$ Ethylenediamine

C_5H_5N Pyridine

The following examples are, however, exceptions :

H_2O Aquo*, NO Nitrosyl,

NH_3 Ammine, CO Carbonyl.

(*d*) *For organic ligands, their names are used as such.* For example,

C_6H_5 Phenyl H_2NCSNH_2 Thiourea

C_5H_5N Pyridine

$P(C_6H_5)_3$ Triphenylphosphine

4. Order of naming ligands. According to *old conventions,* the names of more than one type of ligands surrounding the central atom are written in the order, (*i*) *Negative* (*ii*) *Neutral* (*iii*) *Positive,* without separating them with a hyphen. For the ligands of the same kind present in the co-ordination sphere, the names are written in order of their complexity or alphabetical order. For example, in the complex, $[Co(NH_3)_4Cl(NO_2)]Cl$, the ligands are named in the order chloro, nitro (negative ligands) and ammine (neutral ligand). Thus, the complex $[Co(NH_3)_4Cl(NO_2)]Cl$ is named as **chloronitrotetra amminecobalt(III) chloride.**

According to the latest **IUPAC conventions the** ***names of ligands surrounding the central metal atom are written in alphabetical order of preference irrespective of whether they are negative or neutral.*** For example, in the complex $[Co(NH_3)_4Cl(NO_2)]$, the ligands are named in the order ammine, chloro and nitro. *It must be noted that the prefixes di, tri, etc. are not to be considered while determining the alphabetical order.*

In the present text the **new** *IUPAC system has been followed.*

5. Numerical prefixes to indicate number of ligands. The number of each kind of ligands are specified by the prefixes *di, tri, tetra,* etc. If the ligand is complex, such as ethylenediamine (en), ethylenediaminetetraacetato (edta), etc. and is repeated two, three or four times then the words *bis, tris, tetrakis,* etc., are used followed by the name of the ligand in parentheses. It is illustrated by the examples below :

$[Co(en)_3]Cl_3$ is named as

Tris(ethylenediamine) cobalt(III) chloride

$[Co(H_2NCH_2CH_2NHCH_2CH_2NH_2)_2](NO_3)_3$ is named as

Bis(diethylene triamine) cobalt(III) nitrate

However, when monodentate ligands like methyl amine are repeated, the word bis is used instead of di. It is because if di is used, it becomes dimethylamine which is a different compound.

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**H_2O *is also named as* aqua these days.*

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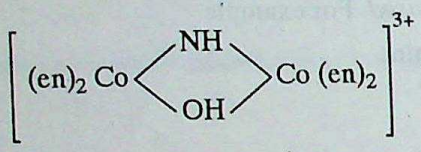
6. Ending of name. *Names of complex cations and neutral molecules have no distinguishing termination but in the case of anionic complexes the suffix "**ate**" is attached to the name of central atom.* For example, the names of some compounds with anionic complexes are :

$K_4[Ni(CN)_4]$ is named as **Potassium tetracyanonickelate(0).**

$Na_3[Co(ox)_3]$ is named as **Sodium tris(oxalato) cobaltate(III).**

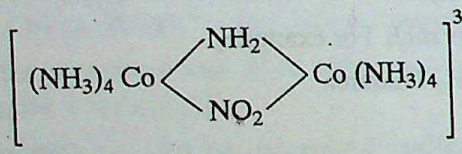
$K_3[Fe(CN)_6]$ is named as **Potassium hexacyanoferrate(III).**

7. Naming of bridging groups. For polynuclear complexes *i.e.*, containing two or more metal atoms, the ligands binding two metal atoms are termed as *bridging ligands.* In naming of such ligands the word μ (mu) is added before the name of such ligands and is separated from the rest of the complex by hyphen (-). For more than one bridging group, the word μ is repeated before each bridging group. For example,



is named as

Bis(ethylenediamine)cobalt(III)-μ-imido-μ-hydroxo bis(ethylenediamine)cobalt(III) ion



$(NO_3)_4$ is named as

Tetraamminecobalt(III)-μ-amido-μ-nitrotetraamminecobalt(III) nitrate.

The names of some co-ordination compounds on the basis of these rules are given below :

Formula	Name
$Ni(CO)_4$	Tetracarbonylnickel (0)
$[Co(NH_3)_6]Cl_3$	Hexaamminecobalt(III) chloride
$[Co(NH_3)_5Cl]Cl_2$	Pentaamminechlorocobalt(III) chloride
$[Cr(H_2O)_4Cl_2]Cl$	Tetraaquodichlorochromium(III) chloride
$K_4[Ni(CN)_4]$	Potassium tetracyanonickelate(0)
$[Co(NH_3)_3(NO_2)_3]$	Triamminetrinitrocobalt(III)
$[Pt(NH_3)_6]Cl_4$	Hexaammineplatinum(IV) chloride
$K_3[Fe(CN)_6]$	Potassium hexacyanoferrate(III)
$[Cr(H_2O)_3(NH_3)_3]Cl_3$	Triamminetriaquochromium(III) chloride
$[Pt(NH_3)_2Cl_2]$	Diamminedichloroplatinum(II)
$K_3[Fe(C_2O_4)_3]$	Potassium tris(oxalato)ferrate(III)
$[Co(NH_3)_5CO_3]Cl$	Pentaamminecarbonatocobalt(III) chloride
$[Ag(NH_3)_2]Cl$	Diamminesilver(I) chloride
$[Co(en)_2Cl_2]_2SO_4$	Dichlorobis(ethylenediamine)cobalt (III) sulphate
$[Co(NH_3)_4(NO_2)Cl]NO_3$	Tetraamminechloronitrocobalt(III) nitrate
$K_3[Ir(C_2O_4)_3]$	Potassium trioxalatoiridate(II)
$Hg(Co(SCN)_4]$	Mercuric tetrathiocyanatocobaltate(II)

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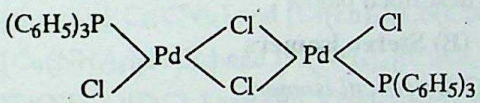
Formula	Name
$\overset{IV}{[Pt(NH_3)_4Cl_2]}\ \overset{II}{[PtCl_4]}$	Tetraamminedichloroplatinum(IV) tetrachloroplatinate(II)
$Na_2[CrOF_4]$	Sodium tetrafluorooxochromate(IV)
$K[BF_4]$	Potassium tetrafluoroborate(III)
$K_2[OsCl_5N]$	Potassium pentachloronitridoosmate(VI)
$[Co(en)_2F_2]ClO_4$	Bis(ethylenediammine)difluorocobalt(III) perchlorate.
$[Co(NH_3)_4Cl_2]_3[Cr(CN)_6]$	Tetraamminedichlorcobalt(III) hexacyanochromate(III)
$[Ag(NH_3)_2]_2SO_4$	Diamminesilver(I) sulphate
$Fe_4[Fe(CN)_6]_3$	Ferric hexacyanoferrate(II)
$[(NH_3)_5Cr—OH—Cr(NH_3)_5]Cl_5$	Pentaamminechromium(III) -μ-hydroxopentaamminechromium(III) chloride
$Na_2[SiF_6]$	Sodium hexafluorosilicate(IV)
	Chlorotriphenylphosphine palladium(II) -μ-dichloro chlorotriphenyl phosphine palladium(II)
$[Mn_3(CO)_{12}]$	Dodecacarbonyltrimanganese(0)
$[Fe(C_5H_5)_2]$	Bis(cyclopentadienyl)iron(II)
$[Pt(py)_4][PtCl_4]$	Tetrapyridineplatinate(II) tetrachloroplatinate(II)
$Cr(C_6H_6)_2$	Bis(benzene) chromium(O)
$Na_3[Ag(S_2O_3)_2]$	Sodium bis(thiosulphate)argentate(I)
$Li(AlH_4]$	Lithium tetrahydridoaluminate(III)

REVIEW QUESTIONS

12.6. Which of the following names are not correct ? Point out the mistakes.

(*i*) $[Cu(H_2O)(NH_3)\ Br_2]$; Amminoaquodibromocopper(I)
(*ii*) $Na_3[Al(C_2O_4)_3]$; Trisodiumtrioxalatoaluminate(III)
(*iii*) $Na_2[Ni(EDTA)]$; Sodium ethylenediaminetetracetatonickel(II)
(*iv*) $[Co(NH_3)_5\ ONO]\ SO_4$; Pentaamminenitrocobalt(III) sulphate

12.7. Write the formula of the following co-ordination compounds

(*i*) Potassium hexanitritoferrate(III)
(*ii*) Dichloroplatinum(IV) tetrachloroplatinate(II)
(*iii*) Bis(acetylacetonato) oxovanadium(IV)
(*iv*) Potassium tetrahydroxozincate(II)
(*v*) Sodium pentacyanonitrosylsulphidoferrate(III)

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12.4. ISOMERISM IN COORDINATION COMPOUNDS

The two or more chemical compounds with identical chemical formula but different structures are called isomers, and the phenomenon is known as isomerism. This phenomenon is not restricted to carbon compounds only but is also found, though less frequently, among inorganic substances.

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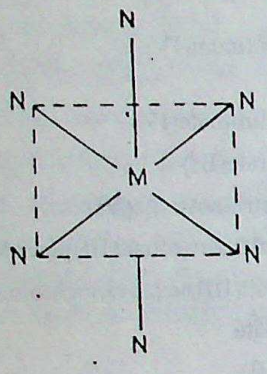
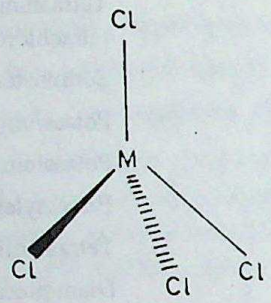
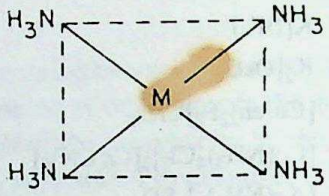
In co-ordination compounds, the ligands are arranged spatially in specific orientation around a given metal atom or ion. Some examples are shown below :



Octahedral



Tetrahedral



Square-planar

Several isomeric possibilities, thus, arise depending upon the position and arrangement of ligands around the metal ion. Isomers can be broadly classified into two major categories : **structural isomers** and **stereoisomers.** Each of these kinds of isomers can be further sub-divided as described below :

(A) Structural isomers

1. *Ionisation isomers*
2. *Co-ordination isomers*
3. *Linkage isomers*
4. *Hydrate isomers*

(B) Stereo isomers

1. *Geometrical isomers*
2. *Optical isomers*

Let us now briefly discuss the different types of isomers.

A. Structural isomers

These are the isomers which have different arrangement of ligands around the central metal atom. The various types of structural isomers are being discussed as follows :

1. Ionisation Isomers

Compounds which have same composition but yield different ions in solution are called **ionisation isomers.** In this type of isomerism, there is an interchange of groups between the co-ordination sphere of the metal ion and the ions outside this sphere. Hence, the two compounds have the same formula but differ with respect to the ionic groups.

For example, violet coloured pentaamminebromocobalt(III) sulphate, $[Co(NH_3)_5Br]SO_4$, is an ionisation isomer of red coloured penta-amminesulphatocobalt(III) bromide, $[Co(NH_3)_5SO_4]Br$.

$[Co(NH_3)_5Br]^{2+}SO_4^{2-}$	and	$[Co(NH_3)_5SO_4]^{+}Br^{-}$
Pentaamminebromo cobalt(III) sulphate (*violet*)		Pentaamminesulphato cobalt(III) bromide (*red*)

The violet compound, in aqueous solutions, gives a precipitate with $BaCl_2$ and not with $AgNO_3$ solution whereas the red compound gives a precipitate with $AgNO_3$ solution and not with $BaCl_2$ solution.

Some other examples are :

$[Pt(NH_3)_4Cl_2]\ Br_2$ and $[Pt(NH_3)_4Br_2]\ Cl_2$

$[Co(NH_3)_5\ NO_3]\ SO_4$ and $[Co(NH_3)_5SO_4]\ NO_3$

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$[Co(NH_3)_5 Br] C_2O_4$ and $[Co(NH_3)_5C_2O_4] Br$

$[Co(NH_3)_4 Cl(NO_2)] Cl$ and $[Co(NH_3)_4Cl_2] NO_2$

$[Cr(NH_3)_5 SO_4] Br$ and $[Cr(NH_3)_5Br] SO_4$.

2. Co-ordination Isomers

This type of isomerism is shown by compounds in which both cation as well as anion are complexes. Here, the isomers differ as a result of different groups being co-ordinated about a particular co-ordination centre. It is shown by the compounds in which cation as well as anion are complexes. For example,

$$[Co(NH_3)_6][Cr(CN)_6] \text{ and } [Cr(NH_3)_6][Co(CN)_6]$$

In the above example, cobalt occurs as a cation in the first and anion in the second whereas the situation of chromium is reversed.

Other examples of this type are cited below :

$[Co(NH_3)_6][Cr(CN)_6]$ and $[Cr(NH_3)_6][Co(CN)_6]$

$[Co(NH_3)_6][Cr(C_2O_4)_3]$ and $[Cr(NH_3)_6][Co(C_2O_4)_3]$

$[Co(en)_3][Cr(CN)_6]$ and $[Cr(en)_3][Co(CN)_6]$

$[Cu(NH_3)_4][PtCl_4]$ and $[Pt(NH_3)_4][CuCl_4]$

$[Pt(NH_3)_4][PtCl_4]$ and $[PtCl(NH_3)_3][PtCl_3(NH_3)]$

$[Cr(NH_3)_6][Cr(CNS)_6]$ and $[Cr(NH_3)_4 (CNS)_2][Cr(NH_3)_2(CNS)_4]$

3. Linkage Isomers

This type of isomers result from two possible ways of attachment of a ligand to the central atom. For example, NO_2 group can bind to the metal either through nitrogen *i.e.*, as a nitro grouping —N<(O, O) or through oxygen atom *i.e.*, as nitrito (—O—N = O) groping. For example,

$[Co(NH_3)_5NO_2]Cl_2$	and	$[Co(NH_3)_5ONO]Cl_2$
Pentaamminenitro cobalt(III) chloride		Pentaamminenitrito cobalt(III) chloride

The unidentate ligands which can bind to the central atom through two possible donor atoms are also called **ambidentate ligands.** Some common examples are :

nitro (—NO_2) and *nitrito (—ONO)*

cyano (—CN) and *isocyano (—NC)*

thiocyanato (—CNS) and *isothiocyanato (—NCS)*

Some more examples of linkage isomers are :

$[Cr(H_2O)_5SCN]^{2+}$ and $[Cr(H_2O)_5NCS]^{2+}$

$[(NH_3)_2(Py)_2Co(NO_2)_2] NO_3$ and $[(NH_3)_2 (Py)_2Co(ONO)_2] NO_3$

$[Mn(CO)_5SCN]$ and $[Mn(CO)_5NCS]$

4. Hydrate Isomers

This type isomerism arises because of capability of water molecules to appear in a variety of ways, inside and outside the co-ordination sphere to give a number of hydrate isomers. For example, there are three hydrate isomers of the formula $CrCl_3.6H_2O$ as shown below :

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$[Cr(H_2O)_6]\ Cl_3$,	$[Cr(H_2O)_5\ Cl]Cl_2.H_2O$	and	$[Cr(H_2O)_4Cl_2]\ Cl.2H_2O$
Hexaaquo chromium(III) chloride (*violet*)	Pentaaquochloro chromium(III) chloride Monohydrate (*blue green*)		Tetraaquodichloro chromium(III) chloride dihydrate (*green*)

Other examples of hydrate isomerism are :

$[Co(NH_3)_4\ (H_2O)\ Cl]Cl_2$ and $[Co(NH_3)_4Cl_2]Cl.H_2O$

$[Co(NH_3)_3\ (H_2O)_2\ Cl]Br_2$ and $[Co(NH_3)_3(H_2O)Cl\ Br]Br.H_2O$

$[Co(NH_3)_4\ (H_2O)\ Cl]\ Br_2$ and $[Co(NH_3)_4\ Br_2]Cl.H_2O$

$[Co(en)_2(H_2O)\ Cl]\ Cl_2$ and $[Co(en)_2Cl_2]Cl.H_2O$

$[Cr(Py)_2\ (H_2O)_2\ Cl_2]\ Cl$ and $[Cr\ (Py)_2(H_2O)Cl_3].H_2O$.

REVIEW QUESTIONS

12.8. Which type of isomerism is shown by the following pairs ?

(*i*) $[Co(NH_3)_4(NO_2)(Cl)]\ Cl$ and $[Co(NH_3)_4Cl_2]\ NO_2$

(*ii*) $[Co(NH_3)_4(CN)_2][Cr(NH_3)_2(CN)_4]$ and $[Co(NH_3)_5(CN)][Cr(NH_3)(CN)_5]$

(*iii*) $[Mn(CO)_5(SCN)]$ and $[Mn(CO)_5(NCS)]$

(*iv*) $[Pt(NH_3)_4][PtCl_6]$ and $[Pt(NH_3)_4Cl_2]\ [PtCl_4]$

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B. Stereoisomers

These isomers contain same atoms and the same atom to atom bonding but differ only in the spatial arrangement of atoms or groups about the central metal atom. It is possible only in the complexes with a co-ordination number four or greater than four. The two important types of stereoisomers are being described as follows :

1. Geometrical Isomers

This type of stereoisomerism arises in the co-ordination compounds due to the difference in geometrical arrangement of the ligands around the central ion. If the same kind of ligands occupy position adjacent to each other, it is called *cis-form* and if these are opposite to each other, it is called *trans-form*. Thus, this kind of isomerism is also referred to as **cis-trans isomerism.**

This type of isomerism is very common in co-ordination complexes with a co-ordination number of 4 and 6.

(*A*) *Isomerism in complexes with co-ordination number 4.* These complexes can either have a tetrahedral or a square planar geometry. The **tetrahedral complexes** do not not show geometrical isomerism because the relative positions of the atoms with respect to each other will be the same. The **square planar complexes** on the other hand show this kind of isomerism as discussed below :

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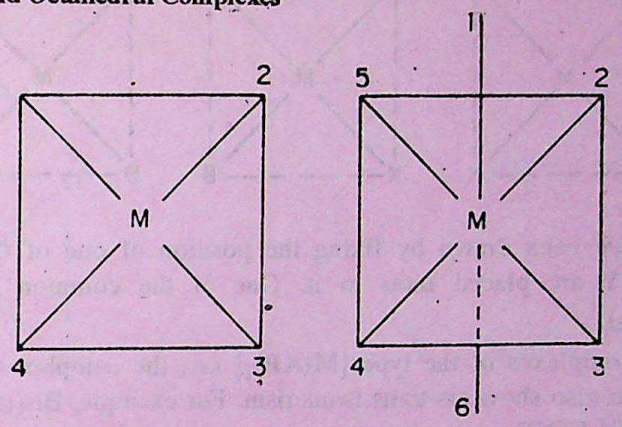
Cis and Trans Positions in

Square plannar and Octahedral Complexes



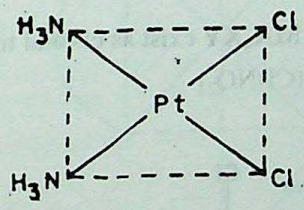
SQUARE PLANAR GEOMETRY OCTAHEDRAL GEOMETRY

In case of *square planar complexes,* the positions 1-4, 2-3, 1-2 and 3-4 are *cis* with respect to each other while the positions 1-3 and 2-4 are *trans* with respect to each other. On the other hand, in octahedral complexes positions 1-6, 2-4 and 3-5 are *trans.*

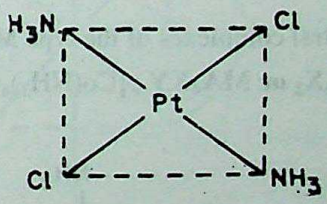
(*i*) Tetra co-ordinated square planar complexes of the type **MA_2X_2, MA_2XY, $MABX_2$** and **MABXY** can exist as cis-trans isomers. Here A and B are *neutral ligands* like $H_2\ddot{O}$: , $\ddot{N}H_3$, CO, NO, $C_5H_5\ddot{N}$, etc., whereas X and Y are *anionic ligands* like Cl^-, NO_2^-, SCN^-, etc.

Some common examples of different types of complexes are as follows :

Type MA_2X_2 : $[Co(NH_3)_2Cl_2]$, $[Pt(NH_3)_2Cl_2]$

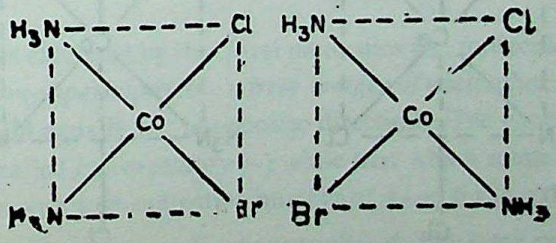


(*Pale yellow*)
cis-isomer



(*Dark yellow*)
trans-isomer

Type MA_2XY : $[Co(NH_3)_2Cl(Br)]$



CIS ISOMER TRANS – ISOMER

Similarly the complex of type **$MABX_2$** will show cis and trans isomers in a similar manner.

Type MABXY : Complexes of this type will have three isomers as shown below.

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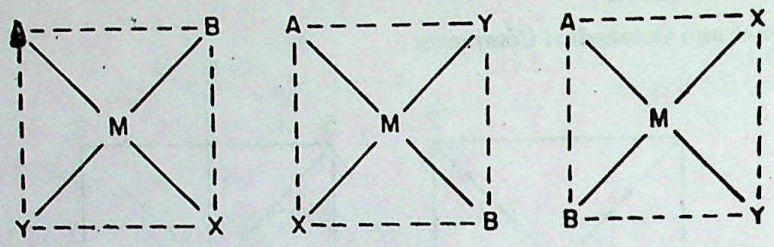
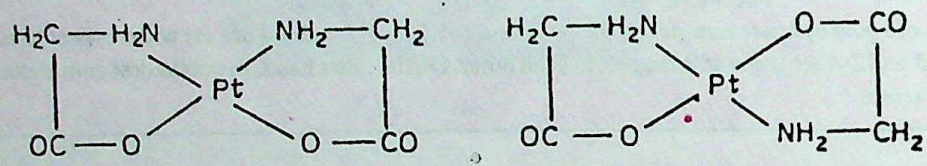


These structures have been drawn by fixing the position of one of the ligand say A while the other ligands B, X and Y are placed trans to it. One of the common example of this type is $[Pt(NH_3)(Py)(NH_2OH)(NO_2)]^+$.

(*ii*) Square planar complexes of the type $[M(AB)_2]$ *i.e.*, the complexes in which unsymmetrical bidentate ligands are present also show cis-trans isomerism. For example, Bis(glycinato)platinum (II) *i.e.*, $[Pt(gly)_2]$. Here gly = $H_2NCH_2COO^-$



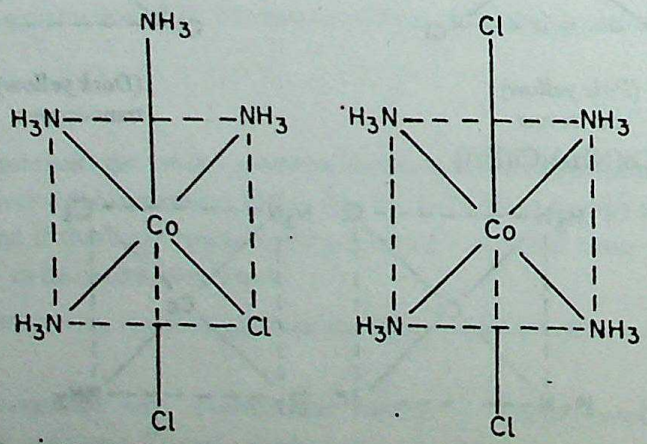
CIS – ISOMER TRANS – ISOMER

It is observed that square planar complexes of the type MA_4, MA_3X, MAX_3 will not show geometrical isomerism because the spatial arrangements for all the above types of complexes will be equivalent.

(*B*) **Isomerism in complexes with co-ordination number 6.** Such complexes have an octahedral geometry. Some common examples of different types of complexes showing this type isomerism are discussed as under.

(*i*) Octahedral complexes of the type MA_4X_2, MA_3X_3, MA_4XY exist as cis and trans isomers.

Type MA_4X_2 or MA_4XY : $[Co(NH_3)_4Cl_2]$, $[Co(NH_3)_4(Cl)NO_2]$



(BLUE OR VIOLET) (GREEN)

CIS – ISOMER TRANS–ISOMER

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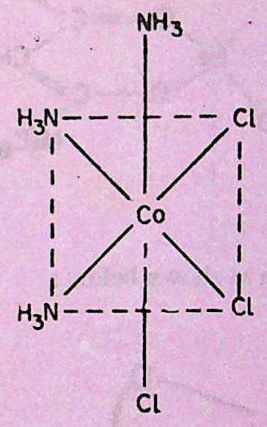
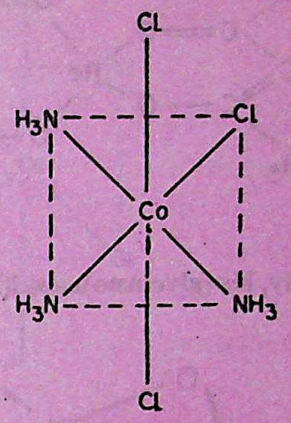
For the complexes of **type MA_3X_3** *e.g.*, $[Co(NH_3)_3Cl_3]$, $[Rh(py)_3Cl_3]$, etc., the isomer is called facial (*fac*) when all the similar ligands occupy the same face of an octahedron as shown below. The other geometric isomer of the compound is called meridional (*mer*).

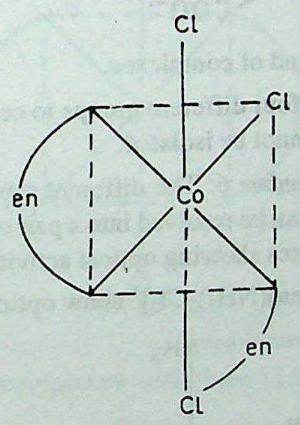


Facial or *fac*-ISOMER

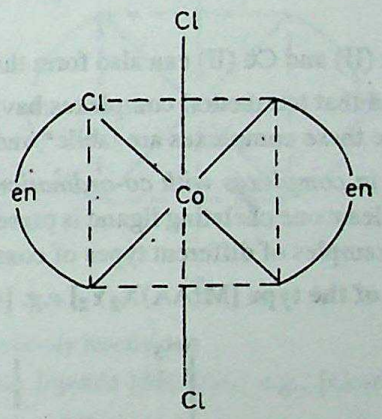


Meridional or *mer*-ISOMER

(*ii*) Complexes of **type $M(AA)_2X_2$** and **$M(AA)_2XY$** can also exist as cis and trans isomers. Here (AA) refers to symmetrical bidentate ligands like ethylene diammine (en) $\ddot{N}H_2CH_2CH_2\ddot{N}H_2$, oxalate ion (ox) $^-OOC—COO^-$, etc., whereas X and Y refer to anonic ligands. Some examples are : $[Co(en)_2Cl_2]^+$, $[Ni(ox)_2Cl_2]^+$, etc.



CIS – ISOMER



TRANS – ISOMER

2. Optical isomers

This type of isomerism is exhibited by the chiral molecules *i.e.*, molecules which do not have plane of symmetry. *These isomers are non-superimposable mirror images of each other.* They are *optically active* and rotate the plane of polarised light equally but in opposite directions. The isomer which rotates the plane of polarised light towards left is called *laevorotatory* (–) while that which rotate plane towards right is called *dextro-rotatory* (+). Complexes with a co-ordination number of 4 and 6 show this kind of isomerism.

(*A*) *Iosmerism in complexes with co-ordination number 4.* ***The tetra co-ordinated complexes with a square planar geometry do not show optical activity because these contain a plane of symmetry.*** However, it has been observed that ***tetrahedral complexes*** which contain unsymmetrical bidentate ligands, $M(AB)_2$ show optical activity. For example, Bis(benzoylacetonato) beryllium(II) gives two optically active forms as shown below :

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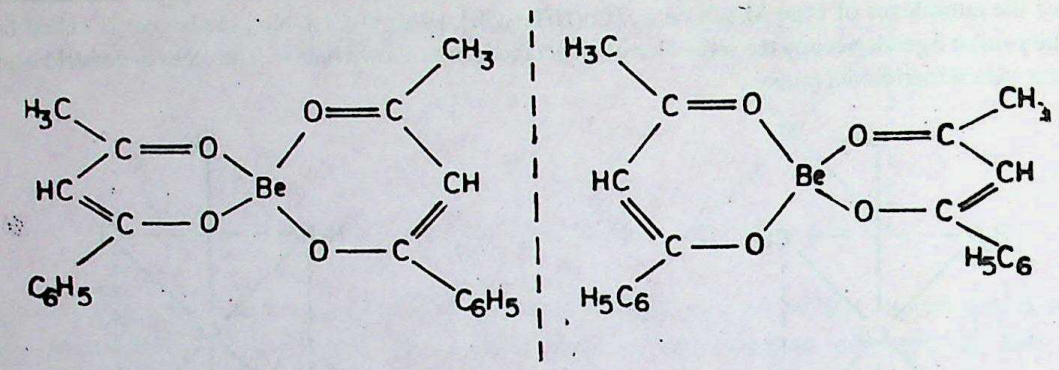
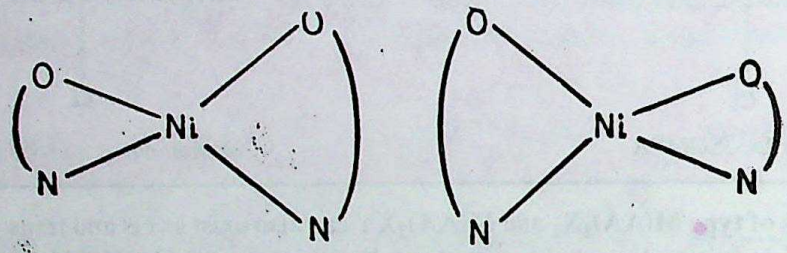


Similarly, bis (glycinato)nickel(II) also exhibits optical isomerism as shown below :



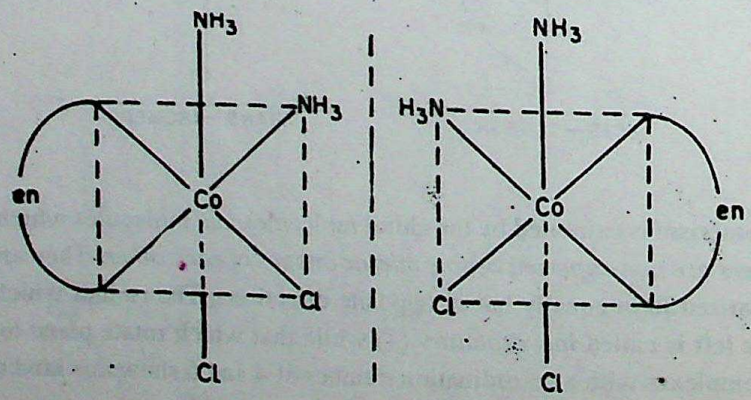
GLYCINATE = CH_2 (bonded to NH_2 and COO^-)

Boron (III), Zn (II) and Cu (II) can also form this kind of complexes.

It must be noted that tetrahedral complexes having four different groups to central atom do not show optical activity because these complexes are labile* and cannot be isolated.

(*B*) *Isomerism in complexes with co-ordination number 6.* The different type of hexa co-ordinated complexes in which at least one chelating ligand is present can be resolved into a pair of enantiomers and have been isolated. Some examples of different types of complexes showing optical activity are discussed below.

(*i*) **Complexes of the type $[M(AA)X_2Y_2]$** *e.g.* $[Co(en)(NH_3)_2Cl_2]^+$ show optical activity.



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(*ii*) Octahedral complexes of the type $[M(AA)_2X_2]$ or $[M(AA)_2XY]$ also show optical activity. Here (AA) = symmetrical bidentate ligand and X, Y are monodentate ligands. Some common examples are $[CO(en)_2Cl_2]^+$, $[Rh(en)_2Cl_2]^+$, etc.

*Labile complexes are the complexes which can easily undergo exchange of ligands.

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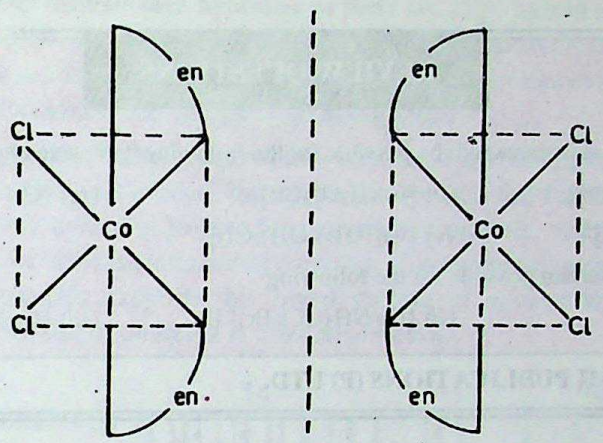
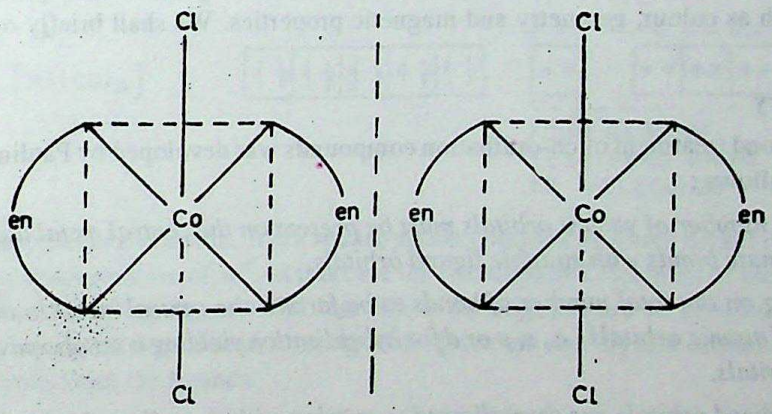


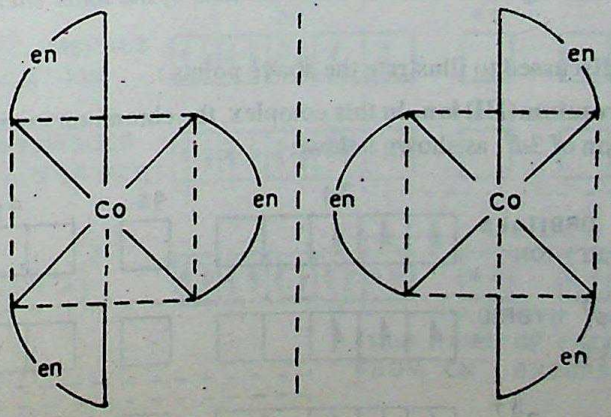
Cis-isomer (*optically active*)

It may not be out of place to mention here that only cis isomer will show optical activity whereas the trans isomer is optically inactive. **Thus, three isomers may be possible in such cases.**



Trans-isomer (optically inactive)

(*iii*) Octahedral complexes with three bidentate ligands $[M(AA)_3]$ *e.g.*, $[Co(en)_3]^{3+}$ will also show optical activity.



Complexes containing hexadentate ligands such as EDTA also show optical isomerism. For example, $[Co(EDTA)]^-$ can be resolved into a pair of enantiomers.

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REVIEW QUESTIONS

12.9. How many geometrical isomers will be possible for the following complexes ?

(*i*) $[PtCl(Py)(NH_3)(Br)]$ (*ii*) $[Co(H_2O)_3Cl_3]$ (*iii*) $[Co(en)_2Cl_2]^+$

(*iv*) $[Cr(en)(NH_3)Cl_3]^+$ (*v*) $[Cr(NH_3)(OH)_2Cl_3]^{2-}$.

12.10. State the kind of isomerism possible for the following

(*i*) $[Cr(en)_3]^{3+}$ (*ii*) $[Cr(NH_3)_4Cl(Br)]\ Br$ (*iii*) $[Cr(NH_3)_4Br_2]_2SO_4$.

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12.5. BONDING IN CO-ORDINATION COMPOUNDS

Werner' theory was the first successful attempt to account for the nature of bonding in case of co-ordination compounds. However, with the development of modern theories like (*i*) *Valence bond theory,* (*ii*) *Ligand field theory,* and (*iii*) *Molecular orbital theory,* it has been possible to explain some properties of these compounds such as colour, geometry and magnetic properties. We shall briefly outline some of these aspects here.

Valence Bond Theory

The valence bond treatment of co-ordination compounds was developed by Pauling. The brief outlines of the theory are as follows :

(*i*) *A suitable number of vacant orbitals must be present on the central metal atom for the formation of co-ordinate bonds with suitable ligand orbitals.*

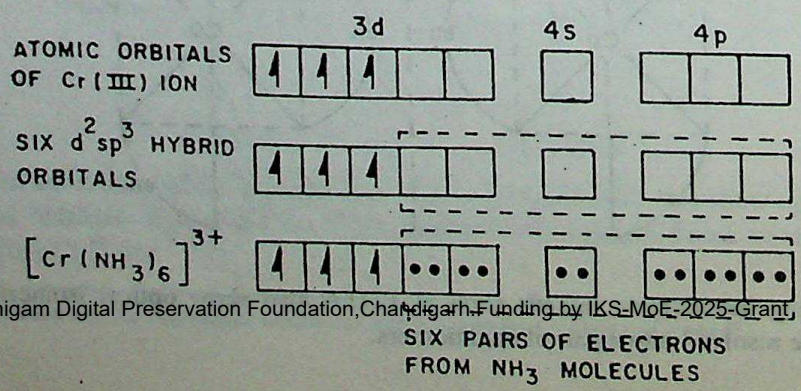
(*ii*) *Depending on the total number of bonds to be formed the central metal ion can use appropriate number of atomic orbitals i.e., s, p or d for hybridisation yielding a set of equivalent orbitals called hybrid orbitals.*

(*iii*) *The hybridised orbitals are then allowed to overlap with those ligand orbitals that can donate an electron pair for bonding.*

(*iv*) *The outer orbital (high spin) or inner orbital (low spin) complexes are formed depending upon whether the d-orbitals of outer shell or the d-orbitals of the inner shell are used in hybridisation scheme.*

A few examples are discussed to illustrate the above points :

(*a*) **Hexaamminechromium(III) ion.** In this complex, the chromium ion is in + 3 oxidation state and has an electronic configuration of $3d^3$, as shown below :



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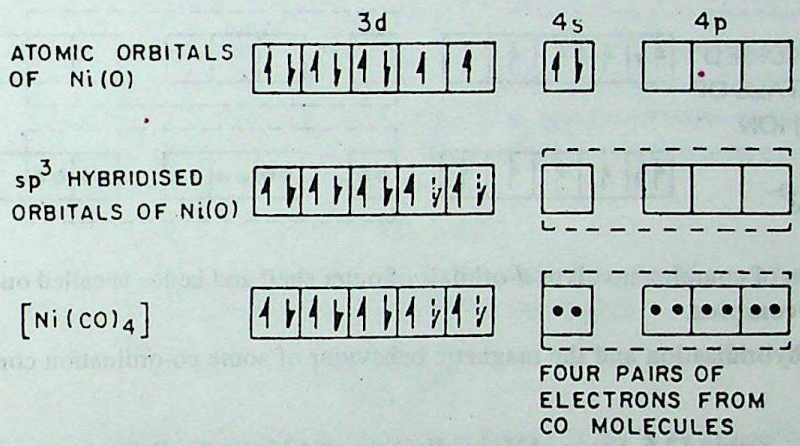
The two $3d$, one $4s$ and three $4p$ orbitals then hybridise to yield six d^2sp^3 hybrid orbitals pointing towards the six ends of an octahedron. The six ammonia molecules then donate a pair of electrons to each of these vacant orbitals. Consequently, the structure of the complex is octahedral. The presence of three unpaired electrons in the remaining orbitals of Cr(III) makes the complex **paramagnetic.**

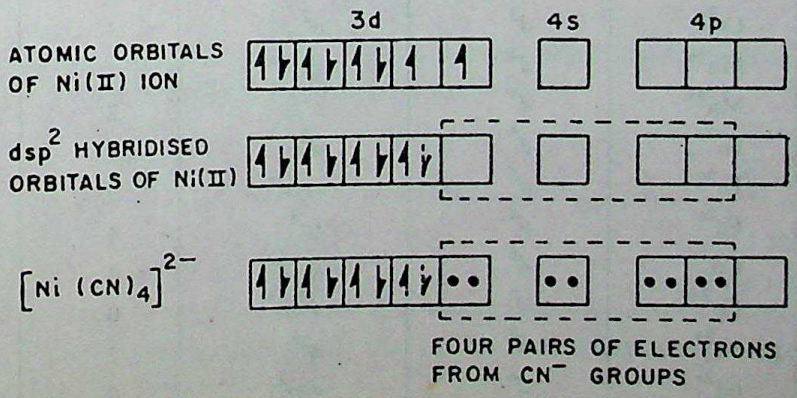
(*b*) **Tetracarbonylnickel(0).** In this complex, the outer electronic configuration of nickel (0) is $3d^8 4s^2$. Under the conditions of formation of chemical bonds the $4s$ electrons are forced to pair with $3d$ electrons. Thus, one s and three p orbitals hybridise to give four equivalent orbitals, oriented tetrahedrally. Each CO group donates a pair of electrons to form a tetrahedral complex. The magnetic studies reveal that the compound is **diamagnetic** in nature and thus supports the forced pairing of $4s$ electrons with $3d$ electrons. The hybridisation scheme and formation of complex is illustrated below :



(*c*) **Tetracyanonickelate(II) ion.** It is a square planar complex in which nickel is in + 2 oxidation state and has the electronic configuration of $3d^8$. In this case the two unpaired electrons of the $3d$ orbitals are forced to pair in the presence of strong ligand, CN^- ion. Since four ligands are to be accommodated, therefore, nickel(II) ion undergoes dsp^2 hybridisation forming four equivalent dsp^2 hybrid orbitals. These accommodate the four pair of electrons from the ligands.

In the formation of the complex since the inner d-orbital is used in hybridisation, $[Ni(CN)_4]^{2-}$ is called an **inner orbital** or **spin paired** or **low spin** or **hyperligated complex.**

The hybridisation scheme is as follows :



As there are no unpaired electrons, the complex is **diamagnetic** and because of dsp^2 hybridisation of nickel it has **square planar geometry.**

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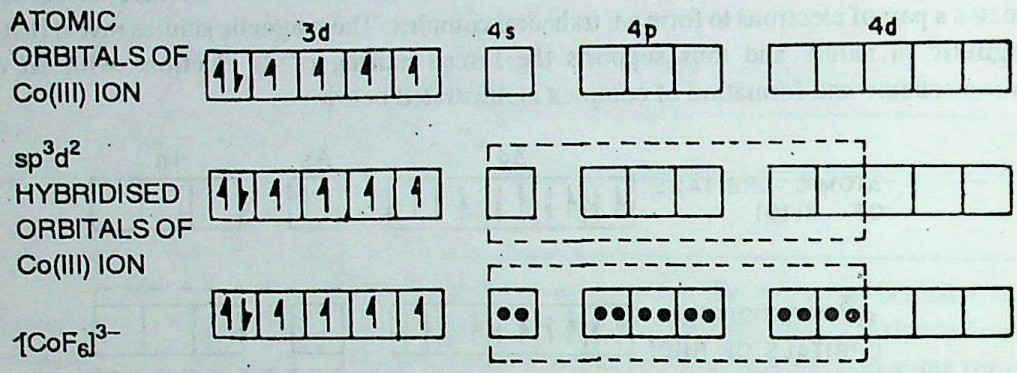
(*d*) **Hexafluorocobaltate(III) ion.** In this complex the outer electronic configuration of cobalt in excited state *i.e.*, under conditions of formation of complexes is $3d^6$. Since F^- ion provides a weak ligand field therefore, one 4*s*, three 4*p* and two 4*d* orbitals hybridise to yield six sp^3d^2 hybrid orbitals pointing towards the six ends of an octahedron. The six F^- ions then donate a pair of electrons to each of these vacant orbitals to have an octahedral geometry. The presence of unpaired electrons in 3*d* orbitals makes the complex **paramagnetic.** The schematic formation of complex is illustrated below :



The formation of complex involves *d*-orbitals of outer shell and hence is called **outer orbital** or **high spin** or **hypoligated complex.**

The state of hybridisation and the magnetic behaviour of some co-ordination complexes is listed in Table 12.5.

Table 12.5. State of Hybridisation and Magnetic Behaviour of Some Co-ordination Complexes

Metal Complex	*Metal ion*	*Configuration of metal ion*	*Hybridisation of metal ion orbitals for ligand bonds*	*Number of unpaired electrons*	*Magnetic behaviour*
$[V(H_2O)_6]^{3+}$	V^{3+}	d^2	d^2sp^3	2	Paramagnetic
$[Cr(NH_3)_6]^{3+}$	Cr^{3+}	d^3	d^2sp^3	3	Paramagnetic
$[MnF_6]^{3-}$	Mn^{3+}	d^4	sp^3d^2	4	Paramagnetic
$[Mn(CN)_6]^{3-}$	Mn^{3+}	d^4	d^2sp^3	2	Paramagnetic
$[Fe(CN)_6]^{3-}$	Fe^{3+}	d^5	d^2sp^3	1	Paramagnetic
$[FeF_6]^{3-}$	Fe^{3+}	d^5	sp^3d^2	5	Paramagnetic
$[FeCl_4]^{2-}$	Fe^{2+}	d^6	sp^3	4	Paramagnetic
$[CoF_6]^{3-}$	Co^{3+}	d^6	sp^3d^2	4	Paramagnetic
$[Co(NH_3)_6]^{3+}$	Co^{3+}	d^6	d^2sp^3	0	Diamagnetic
$[Ni(Cl)_4]^{2-}$	Ni^{2+}	d^8	sp^3	2	Paramagnetic
$[Ni(CN)_4]^{2-}$	Ni^{2+}	d^8	dsp^2	0	Diamagnetic
$[CuCl_4]^{2-}$	Cu^{2+}	d^9	dsp^2	1	Paramagnetic
$[Zn(NH_3)_4]^{2+}$	Zn^{2+}	d^{10}	sp^3	0	Diamagnetic

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The valence bond theory thus, qualitatively, describes bonding in co-ordination compounds. However, the optical *absorption spectra* and *magnetic properties* of the co-ordination complexes could not be explained using this approach. These properties are more satisfactorily explained by the **Ligand Field Theory.**

According to ligand field theory, the approach of the ligands towards the metal atom or ion creates a field. Thus, in the presence of strong ligand field the degeneracy of the *d*-orbitals is lost and they split up into two different sets of orbitals having different energies. The extent of splitting of the metal *d*-orbitals depends on the nature and the number of ligands surrounding the central metal atom. This helps in determining the magnetic and spectroscopic properties of the complexes. A detailed study of the theory is beyond the scope of this book.

12.6. STABILITY OF CO-ORDINATION COMPOUNDS IN SOLUTION

The formation of a co-ordination compound involves reaction between a metal ion and ligands. If the force of attraction of the metal ion with ligands is strong a stable complex may result. Mostly the complex ions are highly stable. However, their possibility of dissociation in aqueous solutions cannot be ruled out completely though these may be dissociated to a small extent. Thus, a chemical equilibrium may be established between the undissociated complex and the dissociated ions.

$$(ML_n)^{b+} \rightleftharpoons M^{a+} + nL^{x-}$$

Here $a+$, $x-$ and $b+$ are the charges on metal atoms, ligand and complex respectively. Thus, the equilibrium constant for the above reaction is given by the expression

$$K = \frac{[M^{a+}][L^{x-}]^n}{[(ML_n)^{b+}]}$$

The above equilibrium constant is called dissociation constant. Consequently, the smaller is the value of K, the greater is the stability of complex and *vice versa.*

The reciprocal of dissociation constant is called stability constant. The greater the value of the stability constant, the greater will be the stability of complex ion.

Alternatively, if the equilibrium is given as

$$M^{a+} + nL^{x-} \rightleftharpoons [ML_n]^{b+}$$

where $a+$, $x-$ and $b+$ have the usual significance, the equilibrium constant Ks, the stability constant of the complex is given as

$$Ks = \frac{[(ML_n)^{b+}]}{[M^{a+}][L^{x-}]^n}$$

The magnitude of the stability constant gives an indication of the *stability of the complex* in solution. The values of Ks for a few complexes in solution are given below :

System	Ks
$Cu^{2+} + 4NH_3 \rightleftharpoons [Cu(NH_3)_4]^{2+}$	4.5×10^{11}
$Cu^{2+} + 4CN^- \rightleftharpoons [Cu(CN)_4]^{2-}$	2.0×10^{27}

The values of Ks given above indicate that CN^- is a relatively stronger ligand than NH_3 and forms more stable complex.

Factors Affecting the Stability of Complex

The stability of a complex depends upon

(*i*) *the nature of central ion and* (*ii*) *the nature of ligand.*

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1. Nature of central ion. The term nature means the charge density on the central ion *i.e.*, greater is the charge density or larger the *charge/radius* ratio, more is the stability of a complex. For example, out of complexes of Fe^{2+} and Fe^{3+}, those of Fe^{3+} are more stable.

For example, $Fe^{3+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{3-}$; $K = 1.2 \times 10^{31}$

$Fe^{2+} + 6CN^- \rightleftharpoons [Fe(CN)_6]^{4-}$; $K = 1.8 \times 10^{6}$

For the ions which carry the same charge the one with a smaller size gives the more stable complexes. For example, among Cu^{2+}, Ni^{2+}, Co^{2+}, Fe^{2+} complexes as the size of copper is the smallest therefore it gives the most stable complexes.

2. Nature of ligand. More basic is a ligand, greater is the ease with which it can donate its electrons and therefore more is the stability of the complex. For example, the complexes involving F^- ions are more stable than those involving Cl^- ions or Br^- ions.

12.7. PREPARATION OF CO-ORDINATION COMPOUNDS

The co-ordination compounds are generally prepared by the following methods :

1. By substitution reactions. A large number of complexes are prepared by this method. In general, this method of synthesis involves the replacement of water molecules or ligands around the metal ion by some other ligands. For example, an aqueous solution of $CuSO_4$ on heating with excess of ammonia gives $[Cu(NH_3)_4]^{2+}$ species having deep blue colour

$$[Cu(H_2O)_4]^{2+} + 4NH_3 \longrightarrow \underset{\text{deep blue}}{[Cu(NH_3)_4]^{2+}} + 4H_2O$$

Some **other examples** *of substitution reactions are* :

$$[Ni(H_2O)_6]^{2+} + 6NH_3 \longrightarrow [Ni(NH_3)_6]^{2+} + 6H_2O$$

$$[Ni(H_2O)_6]^{2+} + 3en \longrightarrow [Ni(en)_3]^{2+} + 6H_2O$$

$$[Co(NO_2)_6]^{3-} + 2en \longrightarrow [Co(en)_2(NO_2)_2]^{+} + 4NO_2^-$$

$$[Ni(NH_3)_4]^{2+} + \underset{\text{dimethyl glyoxime}}{2\ dmg\ H} \longrightarrow \underset{\text{red ppt.}}{Ni(dmg)_2} + 2NH_3 + 2NH_4^+$$

2. By direct combination. Metal ammines can be obtained by direct addition of metal salt to liquid ammonia. A few examples are given below :

$$NiCl_2 + 6NH_3 \longrightarrow [Ni(NH_3)_6]Cl_2$$

$$AgCl + 2NH_3 \longrightarrow [Ag(NH_3)_2]Cl$$

$$CdCl_2 + 4NH_3 \longrightarrow [Cd(NH_3)_4]Cl_2$$

$$CoCl_3 + 6NH_3 \longrightarrow [Co(NH_3)_6]Cl_3$$

Apart from the ammines a number of other complex compounds can be obtained by simple addition reactions. For example,

$$PtCl_2 + 2\ en \longrightarrow [Pt(en)_2]Cl_2$$

$$PtCl_4 + 2KCl \longrightarrow K_2[PtCl_6]$$

$$Ni + 4CO \longrightarrow [Ni(CO)_4]$$

3. By Redox reactions. The complex pentaamminenitratocobalt(III) nitrate can be obtained by reacting cobalt(II) nitrate with concentrated aqueous ammonia and NH_4NO_3 in the presence of H_2O_2.

$$2[Co(H_2O)_6](NO_3)_2 + 8NH_3 + 2NH_4NO_3 + H_2O_2 \longrightarrow 2[Co(NO_3)(NH_3)_5](NO_3)_2 + 14H_2O$$

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Similarly, cobalt(II) chloride can be converted to hexaammine cobalt(III) chloride by treating it with ammonia in the presence of NH_4Cl and H_2O_2.

$$2CoCl_2 + 2NH_4Cl + 10NH_3 + H_2O_2 \longrightarrow 2[Co(NH_3)_6]Cl_3 + 2H_2O.$$

12.8. IMPORTANCE OF CO-ORDINATION COMPOUNDS

The co-ordination compounds are of great importance. These compounds constitute the minerals, plants and are also present in animals. These play important functions. For example, chlorophyll (present in plants) and haemoglobin (essential constituent of blood) are both co-ordination compounds and are of great importance in regulating the various biological functions of plants and animals. Besides these, the co-ordination compounds also find a wider application in the fields of metallurgy, biochemistry, water softening, ion exchange, electrochemistry, textile dyeing, bacteriology and analytical chemistry. For example, EDTA and DMG are required to precipitate metals like Ni, Zn, Cd, etc. Apart from these, the study of complex compounds has enlarged our understanding of chemical bonding, and certain physical properties such as spectral, magnetic properties, etc.

A large variety of co-ordination complexes both naturally existing as well as synthetically prepared are known to us. As the central metal ion is surrounded by different molecular species, these complexes possess different physico-chemical properties and find many applications in different processes. A few **applications** of the **coordination complexes** are summarised below :

1. By complex formation, water insoluble species are brought into solution. For example, in red bauxite Al_2O_3 is separated from Fe_2O_3 by heating with concentrated sodium hydroxide solution. Al_2O_3 dissolves due to the formation of $Al(OH_4)^-$ complex ion.

$$Al_2O_3(s) + 3H_2O(l) + 2OH^-(aq) \longrightarrow 2Al(OH)_4^-(aq)$$

2. In photography, developed film is *fixed* by washing it with a solution of sodium thiosulphate.

$$AgBr(s) + 3Na_2S_2O_3(aq) \longrightarrow Na_3[Ag(S_2O_3)_2](aq) + NaBr(aq)$$

3. The nature of ligands, changes the redox behaviour of the metal ions. For example, in the presence of some ligands cobalt is easily oxidized from + 2 oxidation state to + 3 oxidation state.
4. The hardness of water is estimated by simple titration against EDTA solution. EDTA forms stable complexes with the metal ions present in the hard water. Since stability constants of calcium and magnesium complexes of EDTA are different, even the selective estimation of these ions is possible.
5. Many co-ordination complexes are used as electrolytes for electroplating. These complexes deliver the metal ions in controlled manner. For example, for silver plating the complex $K[Ag(CN)_2]$ is used.
6. Silver and gold are extracted from their respective ores by treatment with sodium cyanide solution. This also involves complex formation.

$$Ag^+(aq) + 2NaCN(aq) \longrightarrow Na[Ag(CN)_2](aq) + Na^+$$
$$Au^+(aq) + 2NaCN(aq) \longrightarrow Na[Au(CN)_2](aq) + Na^+$$

7. Co-ordination complexes also find application in the qualitative as well as quantitative estimation of metal ions. For example, Ni^{2+} ions are estimated as their red complex with dimethylglyoxime (DMG). Ca^{2+} and Mg^{2+} ions are estimated as their complexes with EDTA.
8. The complex of calcium with EDTA is used to treat lead poisoning. Inside the body calcium in the complex is replaced by lead. The more stable Pb-EDTA complex is eliminated in urine.
9. The platinum complex *cis*—$[Pt(NH_3)_2Cl_2]$ known as *cisplatin* is used as an antitumor agent in treatment of cancer.
10. Many natural compounds, exist as co-ordination complexes. For example, haemoglobin (a complex of Fe^{2+}), chlorophyll (a complex of Mg^{2+}) and vitamin B_{12} (a complex of Co^{3+}).

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12.9. ORGANOMETALLIC COMPOUNDS

Organometallic compounds are defined as those compounds in which the carbon atoms of organic groups are directly bonded to metal atoms. The compounds of elements such as boron, phosphorus, silicon, germanium and antimony with organic groups are also included in the organometallics. Many organometallic compounds are important reagents which are used for the synthesis of organic compounds.

Classification of Organometallic Compounds*

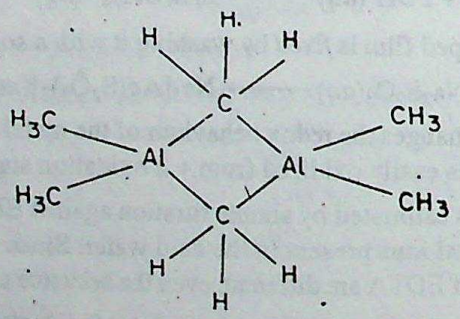
Organometallic compounds can be broadly classified into two categories :

(*a*) σ-*bonded compounds*, and (*b*) π-*bonded compounds*.

σ-Bonded compounds. In these compounds organic group is bonded to a metal atom through a normal 2-electron covalent bond. Some examples of σ-bonded organometallic compounds are given below :

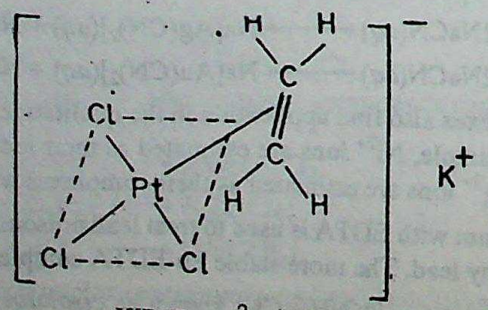
R—Mg—X Grignard reagent (Alkylmagnesium halide)	$(CH_3CH_2)_2Zn$ Diethylzinc
$(CH_3)_4Si$ Tetramethylsilane	$(CH_3)_4Sn$ Tetramethyltin
$(C_2H_5)_4Pb$ Tetraethyllead	$(CH_3)_2Cd$ Dimethylcadmium
n-C_4H_9Li n-Butyllithium	$(CH_3)_3Al$ Trimethylaluminium

Among these, trimethylaluminium exists as stable dimer as shown below. In this, two methyl groups act as bridges between two aluminium atoms. The alkyl bridge is formed by multicentre bonding.



Trimethylaluminium
(Dimer)

π-Bonded organometallic compounds. This type of compounds are generally formed by transition metals. In this type of organometallic compounds the normal σ bond is formed through the π cloud of electrons of the organic molecule. Some examples of π-complexes are



$K[PtCl_3—\eta^2—(C_2H_4)]$
Zeise's Salt
Potassium trichloroethyleneplatinate(II)

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*Classification of organometallic compounds in non-evaluative in CBSE.

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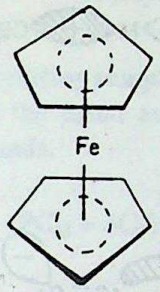
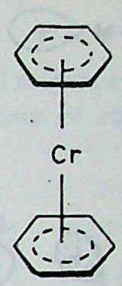


$Fe(\eta^5—C_5H_5)_2$
Ferrocene
Bis (cyclopentaldienyl) iron (II)



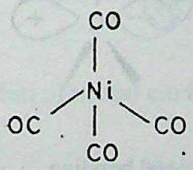
$Cr(\eta^6— C_6H_6)_2$
Dibenzenechromium

Zeise's salt, $K[PtCl_3\eta^2—(C_2H_4)]$ was characterized by Zeise, a Danish pharmacist in about 1830 It is one of the first organometallic compounds of transition metals. In this the plane of the ethylene molecule, the C = C axis are perpendicular to the expected bond direction from the central atom.

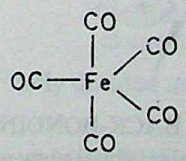
Ferrocene, $Fe(\eta^5—C_5H_5)_2$ was reported in 1951. It possesses a *sandwich* structure in which the iron atom lies between two planar cyclopentadienyl rings. *Dibenzene-chromium*, $Cr(\eta^6—C_6H_5)_2$ also has sandwich structure.

In π-complexes the number of carbon atoms that are bound to the metal atom are indicated by the Greek letter 'η' (*eta*) followed by a number as η^2, η^3, η^4, etc. For example, η^3 means that three carbon atoms are bound to the metal atom.

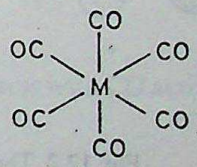
Metal carbonyls of transition metals constitute another important class of organometallic compounds. The first metal carbonyls, $Ni(CO)_4$ and $Fe(CO)_5$ were discovered by A. Mond in 1890 and 1891. Some more examples of metal carbonyls are $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$. In addition to mononuclear metal carbonyls mentioned above, transition metals form many polynuclear metal carbonyls such as $Fe_3(CO)_{12}$, $Mn_2(CO)_{10}$. The metal carbonyl bonds in metal carbonyls possess both σ and π character. Shapes of some typical metal carbonyls are shown below :



$Ni\cdot(CO)_4$



$Fe(CO)_5$



M = Cr, Mo, OR W
$M(CO)_6$

Bonding in Organometallic Compounds*

Bonding in metal carbonyls. As already mentioned, the M—C bond in metal carbonyls has σ as well as π character. The metal-carbon σ bond is formed by the donation of lone pair of electrons on the carbonyl carbon into a vacant orbital of the metal as shown in Fig. 12.1. The metal-carbon π bond is formed by the donation of a pair of electrons from a filled *d*-orbital of metal into the vacant antibonding pi-molecular orbital (π^*) of carbon monoxide.

Bonding in complexes of alkenes. The bonding in these complexes has two components. Firstly, the π-electron density of the alkene overlaps with a σ-type vacant orbital on the metal atom. Secondly, a back-bond is formed by the flow of electron density from a filled *d*-orbital on the metal into the vacant π^*-antibonding molecular orbital on the carbon atoms as shown in Fig. 12.2.

*Bonding in organometallic is not evaluative in CBSE.

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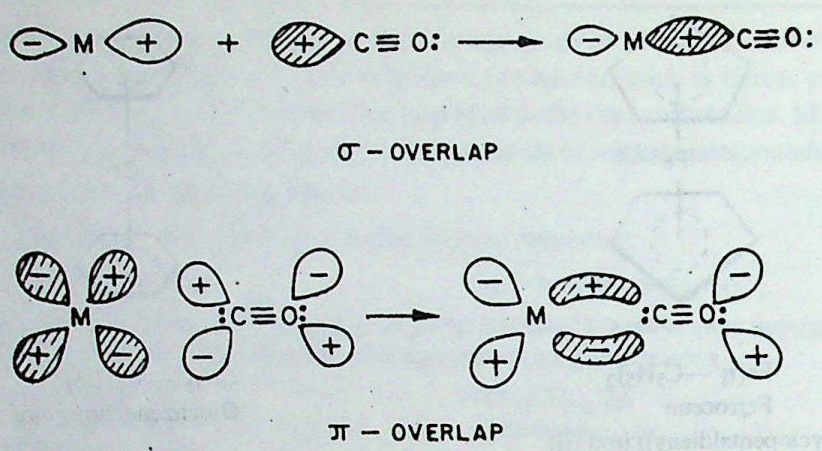

Fig. 12.1. Bonding in metal carbonyls.

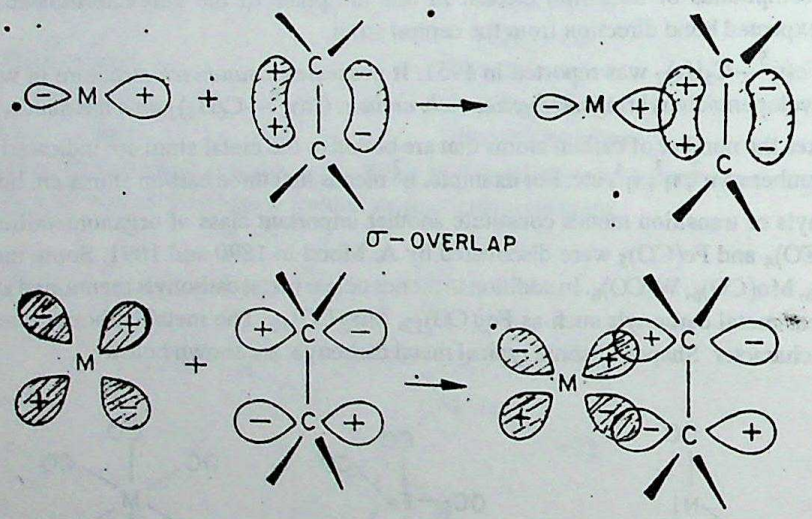

Fig. 12.2. The molecular orbital view of alkene-metal bonding.

Synthesis of Organometallic Compounds

The metal-carbon bonds can be generated in many ways. Some of the important methods are given below :

1. By direct reaction of metals. The metals like Li, Na, K, Mg, Zn and Cd react directly with alkyl halides in the presence of some suitable, solvent such as diethyl ether to form the corresponding organometallic compounds. For example,

$$R—X + Mg \xrightarrow{(C_2H_5)_2O} \underset{\text{Grignard reagent}}{R—Mg—X}$$

$$R—X + 2M \xrightarrow{(C_2H_5)_2O} R—M + MX$$

$$n\text{-}C_4H_9Br + 2Li \xrightarrow{(C_2H_5)_2O} \underset{n\text{-Butyllithium}}{n\text{-}C_4H_9—Li} + LiBr$$

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$$2C_2H_5Br + 2Zn \longrightarrow (C_2H_5)_2Zn + ZnBr_2$$

Diethyl zinc

2. By use of alkylating reagents. The reagents, such as Grignard reagent and alkyllithium reagents on reaction with most of the metal and non-metal halides in the presence of ether as solvent yield other organometallic compounds.

$$PCl_3 + 3C_6H_5MgCl \xrightarrow{\text{Ether}} P(C_6H_5)_3 + 3MgCl_2$$

Triphenyl phosphine

$$CdCl_2 + 2C_2H_5MgCl \xrightarrow{\text{Ether}} (C_2H_5)_2Cd + 2MgCl_2$$

Diethylcadmium

$$SnCl_4 + 4\,n\text{-}C_4H_9Li \longrightarrow (n\text{-}C_4H_9)_4\,Sn + 4LiCl$$

$$PbCl_4 + 4C_2H_5MgBr \longrightarrow (C_2H_5)_4\,Pb + 4MgBrCl$$

Tetraethyllead

3. Preparation of π-complexes. The methods of preparation of a new typical π-complexes are given below :

Preparation of Zeise's salt

$$H_2C = CH_2 + K_2PtCl_4 \longrightarrow [PtCl_3(C_2H_4)]^- K^+ + KCl$$

Zeise's salt

Preparation of ferrocene

$$2C_5H_5MgBr + FeCl_2 \longrightarrow [(C_5H_5)_2Fe] + 2MgBrCl$$

Ferrocene

Preparation of dibenzenechromium

$$2C_6H_6 + Cr\ (\text{vapours}) \longrightarrow [(C_6H_6)_2Cr]$$

Dibenzene-chromium

4. Preparation of metal carbonyls. Finely divided nickel reacts with CO at room temperature to form $Ni(CO)_4$.

$$Ni + 4CO \longrightarrow Ni\,(CO)_4$$

Iron reacts with CO at higher temperature and pressure.

$$Fe + 5CO \longrightarrow Fe\,(CO)_5$$

Nickel can be purified by first converting it into volatile $Ni(CO)_4$ and subsequent thermal decomposition of $Ni(CO)_4$. This process is known as *Mond process*.

Applications of Organometallic Compounds

1. The soluble organometallic complexes of transition metals act as homogeneous catalyst. Some examples are :

   (*a*) Selective hydrogenation of certain double bonds using Wilkinson's catalyst, $(Ph_3P)_3\,RhCl$.

   (*b*) $(Et_3P)_2\,NiCl_2$, acts as catalyst for the isomerization of alkenes.

2. Organometallic compounds can also act as heterogeneous catalyst. For example, Zeigler—Natta catalyst (a solution of $TiCl_4$, containing triethylaluminium) for the polymerization of ethylene and the other alkenes.

3. Organometallic compounds of magnesium (R—Mg—X), cadmium (R_2Cd) and lithium (R—Li) are extensively used in organic synthesis.

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4. Tetraethyl lead is used as an antiknock compound.
5. A number of organometallics also find application in agriculture. For example, ethyl mercury chloride, C_2H_5HgCl is used as a *fungicide* for the protection of young plants and seeds against fungal infection.
6. Aryl arsenic compounds are used as chemotherapeutic agents.
7. Silicon rubbers, because of their high thermal stability, resistance to oxidation and chemical attack, are used in modern surgery for the purpose of production of artificial body parts.

SOME IMPORTANT TERMS AND CONCEPTS

- **Addition Compounds.** The compounds formed by combination of two or more compounds in stoichiometric proportions.
- **Double Salts.** These addition compounds are stable only in solid state but lose their identity in solution form.
- **Coordination Compounds.** These addition compounds retain their identity in solid state as well as in solution form. In these compounds a central atom is bonded to a number of groups through coordinate bonds.
- **Ligands.** An atom or group of atoms that can donate a pair of electrons to the central metal atom. These are called *monodentate, bidentate, tridentate ..... polydentate* depending upon the number of donor sites.
- **Chelating Ligands.** Multidentate ligands are chelating ligands if they can be attached to a particular metal atom simultaneously through two or more than two sites.
- **Coordination Number.** The total number of ligands attached to the central metal atom in the coordination sphere.
- **Isomers.** The compounds having same molecular formula but different structures.
- **Stability constant.** $$K_s = \frac{[(ML_n)^{b+}]}{[M^{a+}][L^{x-}]^n}$$

  Greater the value of K_s more is the stability of the complex.
- **Labile Complex.** A complex in which ligands can be readily replaced by other ligands.
- **Organometallic Compounds.** The compounds in which the carbon atoms of organic groups are directly bonded to metal atom.

  Sigma bonded complexes : CH_3MgBr, $(CH_3)_2Cd$, $(CH_3)_4Sn$, $(C_2H_5)_4Pb$

  Pi bond complexes : Ferrocene, Zeise's salt.

EXERCISE

VERY SHORT-ANSWER QUESTIONS
(1 Mark)

1. What is the charge on the metal atom in the complex ion, $[Co(NH_3)_3(H_2O)_2Cl]^+$?
2. What is the charge of the complex of Pt^{2+} in which the ligands are : one water molecule, one pyridine molecule and one ethylene-diamine molecule ?

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3. Write IUPAC name of $[Co(NH_3)_5Cl]Cl_2$. *(A.I. CBSE 1991)*
4. What is the co-ordination number of metal ion in $[Pt(NH_3)_2C_2O_4]$?
5. Draw the geometric isomers of $[Pt(NH_3)_2Cl_2]$.
6. Give the electronic configuration of Cr^{3+} ion.
7. Identify the ligands in the complex ion, $[Co(en)_2.Cl.ONO]^+$.
8. Draw the geometry of $[Ni(en)_3]^{2+}$.
9. Draw the geometry of *trans*-$[Pt(NH_3)_2Cl_2]$.
10. Give the IUPAC name of $K_3[Co(NO_2)_6]$. *(Pb. PMT 1991)*
11. Give the chemical formula of potassiumhexacyanoferrate(II). *[CBSE (2) 1992]*
12. K_2PtCl_6 is a well known compound but the corresponding Ni compound does not exist. *[CBSE (1) 1992]*
13. Write the chemical formula of nitropentammine cobalt(III) chloride. *(A.I. CBSE 1995)*
14. Write chemical formula of potassium hexacyanoferrate(II). *(CBSE 1995)*

DESCRIPTIVE QUESTIONS
(2—3 Marks)

Coordination Compounds

15. What is meant by the term ligand ? Give example of each of the following ligands.
    (*i*) bidentate (*ii*) unidentate
    (*iii*) hexadentate (*iv*) tetradentate.
16. In what respect does a double salt differ from co-ordination compound ?
17. Illustrate with examples the terms :
    (*i*) Ambidentate ligand (*ii*) chelate and chelating ligand.
18. Name the following compounds/ions IUPAC rules :
    (*i*) $[Co(en)_3]Cl_3$ (*ii*) $[Fe(CN)_6]^{4-}$ (*iii*) $[Ni(NH_3)_6]Cl_2$
    (*iv*) $[Cr(en)_3]Cl_3$ (*v*) $K[PtCl_3(NH_3)]$ (*vi*) $K_3[Al(C_2O_4)_3]$.
19. Explain giving Werner's postulates, the bonding in co-ordination compounds.
20. Explain the following :
    (*i*) Ferrocyanide ion is diamagnetic and ferricyanide ion is paramagnetic.
    (*ii*) Aqueous solution of potassium ferricyanide does not give test for ferric ions.
    (*iii*) $Pt(NH_3)_2Cl_2$ has a square planar geometry but $Ni(CO)_4$ has tetrahedral geometry.
    (*iv*) $[Sc(H_2O)_6]^{3+}$ is colourless while $[Ti(H_2O)_6]^{3+}$ is coloured.
21. Give two methods for the preparation of co-ordination compounds. Give examples in each case.
22. Write names of following complex ions :
    (*i*) $[Mn(H_2O)_6]^{2+}$ (*ii*) $[Fe(CN)_6]^{3-}$ (*iii*) $[Cr(NH_3)_6]^{3+}$.
23. Write does Werner's co-ordination theory account for the non-ionic nature of the complex $CoCl_3.3NH_3$?
24. Give one suitable example along with its IUPAC name for :
    (*i*) Cationic complex (*ii*) Anionic complex (*iii*) Neutral complex.
25. Write the names of the following complexes according to IUPAC system :
    (*a*) $[Pt(NH_3)_4(NO_2)_2]SO_4$ (*b*) $K_4[Ni(CN)_4]$
    (*c*) $[Co(en)_3]Cl_3$ (*d*) $[Pt(NH_3)_4Cl_2][PtCl_4]$

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(*e*) $\left[(NH_3)_4Co\begin{matrix}NH_2\\O_2\end{matrix}Co(NH_3)_4\right](NO_3)_3$ (*f*) $K_3[Fe(CN)_5NO]$.

26. Name the different kinds of isomerism possible in co-ordination complexes, quoting one suitable example in each case.

27. What is meant by the stability of a complex ion ? How is it expressed ?

28. Name the type of isomerism exhibited by the following pairs :

(*a*) $[Co(en)_2(NO_2)Cl]SCN$ and $[Co(en)_2(NO_2)(SCN)]Cl$ (*b*) $[Co(en)_2(ONO)_2]$ and $[Co(en)_2(NO_2)_2]$

(*c*) $[Cr(NH_3)_6][Cr(CNS)_6]$ and $[Cr(NH_3)_4(CNS)_2][Cr(NH_3)_2(CNS)_4]$.

29. Write down the formulae of the following co-ordination compounds :

(*i*) hexaamminecobalt(III) chloride (*ii*) potassiumhexacyanoferrate(III)

(*iii*) dichlorotetraamminecobalt(III) ion (*iv*) dichlorobis(ethylene diamine) cobalt(III) ion

(*v*) hexaaquochromium(III) chloride (*vi*) hexaammineplatinum(IV) chloride ***(CBSE 1993)***

(*vii*) sodium(ethylenediamminetetracetato)chromate(II). ***(CBSE 1993)***

30. What is meant by isomerism ? Give examples of each of the following in relation to co-ordinate compounds :

(*i*) ionization isomerism (*ii*) linkage isomerism

(*iii*) geometrical isomerism (*iv*) optical isomerism.

31. Giving suitable examples discuss the geometrical shapes associated with the types of hybrid orbitals :

(*a*) sp^3 (*b*) dsp^2 (*c*) d^2sp^3.

32. Explain giving a suitable reason why $[CoF_6]^{3-}$ gives a high spin complex ?

33. Give the ionisation isomers of each of the following compounds. Also name each of them.

(*a*) $[Cr(NH_3)_4I_2]Br$ (*b*) $[Fe(NH_3)_5CN]SO_4$.

34. How many geometrical isomers can exist for the following species ?

(*a*) $[Pt(NH_3)_2Cl_2]$ (*b*) $[Co(NH_3)_3Cl_3]$

(*c*) $[Zn(NH_3)_2Cl_2]$ (*tetrahedral*) (*d*) $[Co(NH_3)(en)Cl_3]$.

35. Predict which among the following are inner or outer orbital and diamagnetic or paramagnetic species

(*a*) $[Cu(H_2O)_6]^{2+}$ (*b*) $[CrCl_4Br_2]^{3-}$ (*c*) $[Co(CN)_6]^{3-}$

(*d*) $[Cr(NH_3)_6]^{3+}$ (*e*) $[MnF_6]^{3-}$.

36. Give the systematic names of the following compounds :

(*a*) $[Co(en)_2Cl_2]I$ (*b*) $(NH_4)_3[CuCl_5]$

(*c*) $Na_2[Co(H_2O)_2(OH)_4]$ (*d*) $K_4[NiF_6]$.

37. Discuss briefly the structure of the following compounds on the basis of valence bond theory :

(*a*) $[Fe(H_2O)_6]^{2+}$ (*b*) $[Fe(CN)_6]^{3-}$.

38. Explain geometrical isomerism with reference to octahedral complexes giving at least two example (hypothetical examples are not required).

39. Square planar complexes with a co-ordination number of four exhibit geometrical isomerism whereas tetrahedral complexes do not, why ?

40. Write the formulae of the following complexes :

(*a*) Trans-chloronitrodiammineplatinum(II)

(*b*) Tetramminecobalt(III)-μ-amido-μ-nitrotetraamminecobalt(III) nitrate

(*c*) Sodium dithiosulphatoargentate(I) (*d*) Dichlorobis(ethylene diamine)cobalt(III) sulphate

(*e*) Chloronitrodiamminecobalt(III) dicyanoaurate(I)

(*f*) Potassium trioxalato ferrate(III)

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[A.I. CBSE (O) 1992]

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(*g*) Nitropentaamminecobalt(III) nitrate [*A.I. CBSE (3) 1992*]

(*h*) Diamminechloroethylenediaminenitroplatinum(IV) chloride.

41. $[NiCl_4]^{2-}$ is paramagnetic while $[Ni(CO)_4]$ is diamagnetic though both are tetrahedral. Explain.

42. Explain why a chelated complex is more stable than an unchelated complex ?

43. (*a*) Explain what is meant by organometallic compounds.

(*b*) Discuss important application of co-ordinate compounds with special reference to

(*i*) extraction of metals (*ii*) analytical chemistry.

44. Using valence bond theory of complexes, explain the geometry and diamagnetic nature of the ion $[Co(NH_3)_6]^{3+}$ (Atomic number of Co = 27). (*A.I. CBSE 1991*)

45. By the help of valence bond theory explain whether $[Ni(CN)_4]^{2-}$ is square planar or tetrahedral in nature. (*Pb. S.B. 1991*)

46. Discuss the bonding in $[Fe(CN)_6]^{3-}$ and $[FeF_6]^{3-}$. (*Pb. S.B. 1992*)

47. Give IUPAC names of

(*i*) $K_3[Fe(C_2O_4)_3]$ (*ii*) $[Co(en)_2Cl_2]SO_4$. (*Har. Sc. 1992*)

48. $K_2[PtCl_6]$ is a well known compound whereas corresponding nickel compound is not known, why ? [*A.I. CBSE (O) 1993*]

49. (*a*) Predict the shape of $[Cr(NH_3)_6]^{3+}$ ion on the basis of valence bond theory.

(*b*) Explain how the nature of ligand affects the stability of a complex ion ? (*Pb. Board 1993*)

50. Give a chemical test to distinguish between $[CO(NH_3)_5Br]SO_4$ and $[CO(NH_3)_5SO_4]Br$. What kind of isomerism do they exhibit ? (*A.I. CBSE 1995*)

51. Explain how $[Pt(NH_3)_2Cl_2]$ and $[Pt(NH_3)_6]Cl_4$ will differ in their electrolytic conductances. Give the hybridisation state of Pt in these compounds. (*CBSE 1995*)

52. Write the formulae of the following complexes.

(*i*) Pentaamminechlorocobalt(III) (*ii*) Lithium tetrahydro aluminate(III) (*I.I.T. 1997*)

53. Write the IUPAC name of the compound $[Cr(NH_3)(NCS)][ZnCl_4]$. Is this compound coloured ? (*I.I.T. 1997*)

Organometallic Compounds

54. Write the structure of each of the following :

(*i*) Ferrocene (*ii*) Zeise's salt

(*iii*) $W(CO)_6$ (*iv*) Dibenzene chromium.

55. Give one method of preparation for each of the following :

(*i*) Tetraethyllead (*ii*) *n*-Butyllithium (*iii*) Diethylcadmium

(*iv*) Ferrocene (*v*) $Ni[CO]_4$ (*vi*) Zeise's salt.

56. Describe the bonding in metal carbonyls.

57. Give the application of organometallic compounds in the following areas :

(*i*) Homogeneous catalysis (*ii*) Heterogeneous catalysis

(*iii*) Organic synthesis.

58. Describe nature of bonding in metal carbonyls. (*CBSE 1992*)

59. Give one method of preparation of π complexes. (*CBSE 1992*)

60. Give the name of co-ordination isomers of the complex $[Co(en)_3][Cr(CN)_6]$. (*CBSE 1997*)

61. How would you prepare tetraalkyl lead ? (*Pb. Board 1997*)

62. Give the oxidation state and outer electronic configuration of $[Ni(CO)_4]^{-1}$ (*Pb. Board 1997*)

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FOR THE COMPETITIVE EXAMS

MULTIPLE CHOICE QUESTIONS

Select the correct answer for the following questions :

1. The oxidation number of Cr in $Na[Cr(NH_3)_2F_4]$ complex is
   (*a*) II (*b*) III
   (*c*) IV (*d*) VI.
2. The formula of potassium dicyanobis(oxalato)nickelate(II) is
   (*a*) $K_4[Ni(CN)(Ox)_2]$ (*b*) $K_3[Ni_2(CN)_2(Ox)_2]$
   (*c*) $K_4[Ni(CN)_2(Ox)_2]$ (*d*) $K_2[Ni(CN)_2(Ox)_2]$.
3. The name of $[Co(NH_2)_3(NO_2)_3]$ is
   (*a*) Trinitrotriamminecobalt(III) (*b*) Trinitrotriamminecobalt(II)
   (*c*) Trinitrotriamminecobalt(III) ion (*d*) Trinitrotriamminecobaltate(III).
4. The co-ordination number of cobalt in the complex $[Co(en)_2Br_2]Cl_2$ is
   (*a*) 4 (*b*) 6 (*c*) 5 (*d*) 2.
5. The number of halide ions in $[Pt(NH_3)_3Cl_2Br]Cl$ will be
   (*a*) 4 (*b*) 3 (*c*) 2 (*d*) 1.
6. $K_3[Al(C_2O_4)_3]$ is called
   (*a*) Potassium alumino oxalate (*b*) Potassium aluminium(III) trioxalate
   (*c*) Potassium trioxalato aluminate(III) (*d*) Potassium tris (oxalato) aluminium.
7. The cation that does not form an ammine complex with excess of ammonia is
   (*a*) Ag^+ (*b*) Al^{3+} (*c*) Cu^{2+} (*d*) Cd^{2+}.
8. EDTA combines with cations to form
   (*a*) chelates (*b*) clathrates
   (*c*) non-stoichiometric compounds (*d*) polymers.
9. One among the following is an example of hexadentate ligands
   (*a*) 2, 2′-bipyridyl (*b*) ethylenediammine tetra acetate ion
   (*c*) dimethyl glyoxime (*d*) iminodiacetate ion.
10. One among the following is not an organometallic compound
    (*a*) Trimethyl boron (*b*) Trimethyl aluminium
    (*c*) Trimethoxy titanium chloride (*d*) Tetracarbonyl nickel.
11. The correct structural formulae of Zeise's salt is
    (*a*) $K^+[PtCl_3(C_2H_4)]^-$ (*b*) $K^+[PtCl_2\text{-}\eta^2\text{-}(C_2H_4)]Cl^-$
    (*c*) $K_2[PtCl_3\text{-}\eta\text{-}C_2H_4]$ (*d*) $K^+[PtCl_3\text{-}\eta^2\text{-}(C_2H_4)]^-$.
12. Amongst $Ni(CO)_4$, $[Ni(CN)_4]^{2-}$ and $NiCl_4^{2-}$
    (*a*) $Ni(CO)_4$ and $NiCl_4^{2-}$ are diamagnetic and $[Ni(CN)_4]^{2-}$ is paramagnetic.
    (*b*) $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $Ni(CO)_4$ is paramagnetic.

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(c) $Ni(CO)_4$ and $[Ni(CN)_4]^{2-}$ are diamagnetic and $NiCl_4^{2-}$ is paramagnetic.

(d) $Ni(CO)_4$ is diamagnetic and $NiCl_4^{2-}$ and $[Ni(CN)_4]^{2-}$ are paramagnetic. *(I.I.T. 1991)*

13. Which of the following coordination compounds can exhibit coordination isomerism ?

(a) $[Co(en)_2Cl_2]Br$ (b) $[Co(NH_3)_6][Cr(CN)_6]$

(c) $[Co(en)_3]Cl_3$ (d) $[Co(NH_3)_5NO_2]Cl_2$.

14. Which of the following compounds can exhibit linkage isomerism ?

(a) $[Co(en)_3]Cl_3$ (b) $[Co(en)_2Cl_2]Cl$

(c) $[Co(en)_2NO_2Cl]Br$ (d) $[Co(NH_3)_5Cl]Br_2$.

15. Which of the following ligands is a bidentate ligand ?

(a) Py (b) Bipy (c) dien (d) EDTA.

16. Which of the following ligands is a tridentate ligand ?

(a) DMG (b) Bipy (c) acac (d) dien.

17. In $Ni(CO)_4$, the nickel atom is ..... hybridised.

(a) sp^2 (b) sp^3 (c) dsp^2 (d) sp^3d.

18. Ziegler-Natta catalyst is $TiCl_3$ dissolved in

(a) Triethylaluminium (b) Ether (c) Water (d) Ammonia.

19. Which of the following compounds can show optical isomerism ?

(a) *trans*-$[Co(en)_2Cl_2]Br$ (b) $[Co(en)_3]Cl_3$

(c) *trans*-$[Co(NH_3)_4Cl_2]Cl$ (d) $[Co(NH_3)_5Cl]Cl_2$.

20. How many ions are produced from $[Co(NH_3)_5Cl]Cl_2$ in solution

(a) 3 (b) 4 (c) 2 (d) 5.

21. The oxidation number of cobalt in $K[Co(CO)_4]$ is

(a) + 1 (b) + 3 (c) – 1 (d) – 3.

(CEET Kurukshetra 1996)

22. The reagent used for identifying Ni^{2+} ions in solution is

(a) Potassium ferrocyanide (b) Dimethylglyoxime

(c) Phenol phthalein (d) EDTA.

23. Which of the following is π-acid ligand ?

(a) NH_3 (b) CO (c) F^- (d) ethylenediamine.

(CEET Kurukshetra 1997)

24. Which of the following is an organometallic compound ?

(a) $Ti(C_2H_4)_4$ (b) $Ti(OC_2H_5)$ (c) $Ti(OCOCH_3)_4$ (d) $Ti(OC_6H_5)$.

(A.I.I.M.S. 1997)

25. The oxidation state of Fe in brown ring complex $[Fe(H_2O)_5NO]SO_4$

(a) + 1 (b) + 2 (c) + 3 (d) + 4. *(A.I.I.M.S. 1997)*

26. Which of the following is an organometallic compound ?

(a) Lithium methoxide (b) Lithium acetate

(c) Lithium dimethylamide (d) Methyl lithium. *(I.I.T. 1997)*

27. The formula of dichlorobis urea copper (II) sulphate is

(a) $[Cu\{O = C(NH_2)_2\}]Cl_2$ (b) $[CuCl_2\{O = C(NH_2)_2\}]$

(c) $[Cu\{O = C(NH_2)_2\}]Cl$ (d) $[CuCl_2\{O = C(NH_2)_2\}_2]$. *(CBSE Ent. 1997)*

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ASSERTION REASON TYPE QUESTIONS

In each of the following questions two statements are given. One labelled as *Assertion A* and other labelled as *Reason R*. Examine the statement carefully and mark the correct answer (*a*), (*b*), (*c*) or (*d*) according to the following instructions.

(*a*) if both A and R are correct and R is correct explanation of A

(*b*) it both A and R are correct but R is not the explanation of A

(*c*) if A is correct but R is wrong

(*d*) if A is wrong and R is correct.

28. ***Assertion A*** : Bisglycinatonickel (II) can show optical isomerisms.

Reason R : Tetrahedral complexes with chiral structure exhibit optical isomerism.

(*a*) (*b*) (*c*) (*d*)

29. ***Assertion A*** : Bisglycinatoplatinum (II) cannot show optical isomerism.

Reason R : Bisglycinatoplatinum (II) is a tetrahedral complex.

(*a*) (*b*) (*c*) (*d*)

30. ***Assertion A*** : $[Co(NH_3)_3Cl_3]$ gives white precipitate with $AgNO_3$ solution.

Reason R : Chlorine is not present in ionisable part of the given complex.

(*a*) (*b*) (*c*) (*d*)

31. ***Assertion A*** : EAN of Fe in its complexes is always 36.

Reason R : Oxidation state of Fe in $Fe(CO)_5$ is 0.

(*a*) (*b*) (*c*) (*d*)

32. ***Assertion A*** : Zeise's salt is organometallic compound.

Reason R : Zeises salt contain C_2H_4 molecule as one of the ligand.

(*a*) (*b*) (*c*) (*d*)

FILL IN THE BLANKS

1. The correct IUPAC name of $K_2[Cu(CN)_4]$ is ..... .
2. The chemical name of the compound $[C_4H_4Fe(CO)_3]$ is ..... .
3. The oxidation number of cobalt in $[Co(EDTA)]^-$ is ..... .
4. $[Cr(NH_3)_6]^{3+}$ is an ..... orbital complex and ..... in nature.
5. The structural formula of cis-dibromochlorotriaquochromium(III) is ..... .
6. The formula of ferrocene is ..... .
7. Grignard's reagent is an ..... .
8. The number of geometrical isomers possible for the complex $[Rh(NH_3)_3Cl]$ are ..... .
9. The co-ordination isomer of the complex $[Co(NH_3)_6][Cr(CN)_6]$ is ..... .
10. In $Ni(CO)_4$ the M—C bond consists of ..... and ..... bond.

TRUE/FALSE STATEMENTS

1. Ethylene diamine is a bidentate ligand.

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2. $EDTA^{4-}$ is a tetradentate ligand.
3. Oxidation state of nickel in $Ni(CO)_4$ is + 4.
4. Chelates are less stable than ordinary coordination complexes.
5. $[Cr(NH_3)_5NO_2]Cl_2$ can exhibit linkage isomerism.
6. *trans*-$[Co(NH_3)_4Cl_2]Cl$ can exhibit optical isomerism.
7. Grignard reagent is an organometallic compound of magnesium.
8. Ferrocene has sandwich structure.
9. Oxidation number of iron in ferrocene is zero.
10. Cisplatin is used as an antitumor drug.

ANSWERS/HINTS

REVIEW QUESTIONS

12.1. (*i*) + 4, (*iii*) + 2, (*iii*) 0, (*iv*) + 1 **12.2.** (*i*) 6, (*ii*) 6, (*iii*) 6, (*iv*) 3
12.3. (*i*) 2 mol, (*ii*) zero, (*iii*) 1 mol, (*iv*) 3 mol
12.5. incorrect names are (*i*), (*ii*) and (*iv*) **12.6.** (*i*) 36, (*ii*) 35, (*iii*) 38, (*iv*) 36
12.7. (*i*) $K_3[Fe(ONO)_6]$, (*ii*) $[PtCl_2][PtCl_4]$, (*iii*) $[VO(acac)_2]$, (*iv*) $K_2[Zn(OH)_4]$, (*v*) $Na_4[Fe(CN)_5NOS]$
12.8. (*i*) ionisation (*ii*) Co-ordination (*iii*) Linkage (*iv*) Co-ordination
12.9. (*i*) 3, (*ii*) 2, (*iii*) 2, (*iv*) 2, (*v*) 2
12.10. (*i*) optical, (*ii*) geometrical, (*iii*) geometrical.

VERY SHORT-ANSWER QUESTIONS

1. + 2 **2.** + 2 **3.** Pentaamminechlorocobalt(III) chloride
4. 4 **10.** Potassium hexanitrocobaltate(III)
13. $[Co(NH_3)_5.ONO]Cl_2$ **14.** $K_4[Fe(CN)_6]$.

DESCRIPTIVE QUESTIONS

18. (*i*) Tris(ethylenediamine)cobalt(III) chloride (*ii*) Hexacyanoferrate(II) ion
(*iii*) Hexaamminenickel(II) chloride (*iv*) Tris(ethylenediamine)chromium(III) chloride
(*v*) Potassium amminetrichloroplatinate(IV)
(*vi*) Potassium trioxalatoaluminate(III).

22. (*b*) (*i*) Hexaquomanganese(II) ion (*ii*) Hexacyanoferrate(III) ion
(*iii*) Hexaamminechromium(III) ion.

25. (*a*) Tetraamminedinitroplatinum(IV) sulphate (*b*) Potassium tetracyanonickelate(0)
(*c*) Tris(ethylenediamine)cobalt(III) chloride
(*d*) Dichlorotetraammineplatinum(IV)tetrachloroplatinate(II)
(*e*) Tetraaminecobalt(III)-μ-amino-μ-peroxotetraamminecobalt(III) nitrate
(*f*) Potassiumpentacyanonitrosylferrate(II).

28. (*a*) ionisation (*b*) linkage (*c*) co-ordination.
29. (*i*) $[Co(NH_3)_6]Cl_3$ (*ii*) $K_3[Fe(CN)_6]$ (*iii*) $[Co(NH_3)_4Cl_2]^+$
(*iv*) $[Co(en)_2Cl_2]^{2+}$ (*v*) $[Cr(H_2O)_6]Cl_3$.

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33. (*a*) $[Cr(NH_3)_4I(Br)]I$ (*b*) $[Fe(NH_3)_5SO_4](CN)$

34. (*a*) two (*b*) three (*c*) zero (*d*) three

35. (*a*) outer, paramagnetic (*b*) inner, paramagnetic (*c*) inner, diamagnetic
(*d*) outer, paramagnetic (*e*) outer, paramagnetic

36. (*a*) Dichlorobis(ethylene diamine)cobalt(III) iodide (*b*) Ammoniumpentachlorocuprate(II)
(*c*) Sodiumdiaquotetrahydroxocobaltate(II) (*d*) Potassiumhexafluoronickelate(II)

40. (*a*) $[Pt(NH_3)_2Cl(NO_2)]$ (*b*) $\left[(NH_3)_4Co\begin{matrix}NH_2\\NO_2\end{matrix}Co(NH_3)_4\right](NO_3)_4$

(*c*) $Na[Ag(S_2O_3)_2]$ (*d*) $[Co(en)_2Cl_2]SO_4$ (*e*) $[Co(NH_3)_2Cl(NO_2)][Au(CN_2)]$
(*f*) $K_3[Fe(C_2O_4)_3]$ (*g*) $[Co(NH_3)_5NO_2](NO_3)_2$ (*h*) $[Pt(NH_3)_2Cl\ en\ NO_2]Cl_2$

47. (*i*) Potassiumtrioxalatoferrate(III) (*ii*) Dichlorobis(ethylenediamine)cobalt(III) sulphate

48. It is because due to a large value of the four ionisation energies, nickel is not known to exist in Ni(IV) state.

49. (*a*) octahedral, sp^3d^2 hybridisation, outer orbital complex (*b*) *refer to Section 12.6.*

MULTIPLE CHOICE QUESTIONS

1. (*b*)	**2.** (*c*)	**3.** (*a*)	**4.** (*b*)	**5.** (*d*)	**6.** (*c*)
7. (*b*)	**8.** (*a*)	**9.** (*b*)	**10.** (*c*)	**11.** (*d*)	**12.** (*c*)
13. (*b*)	**14.** (*c*)	**15.** (*b*)	**16.** (*d*)	**17.** (*b*)	**18.** (*a*)
19. (*b*)	**20.** (*a*)	**21.** (*c*)	**22.** (*b*)	**23.** (*b*)	**24.** (*a*)
25. (*b*)	**26.** (*d*)	**27.** (*b*)	**28.** (*a*)	**29.** (*c*)	**30.** (*d*)
31. (*d*)	**32.** (*a*).				

FILL IN THE BLANKS

1. Potassium tetracyanocuprate(II) **2.** Butadienetricarbonyliron(0) **3.** + 3
4. inner, paramagnetic **5.** $[Cr(H_2O)_3ClBr_2]$ **6.** $(C_5H_5)_2Fe$
7. organometallic compound **8.** three **9.** $[Cr(NH_3)_6][Co(CN)_6]$
10. σ, π

TRUE/FALSE STATEMENTS

1. True	**2.** False	**3.** False	**4.** False	**5.** True	**6.** False
7. True	**8.** True	**9.** False	**10.** True.		

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13

Nuclear Chemistry

LEARNING OBJECTIVES

In this unit, we shall learn :

- *Nature of radiations from Radioactive substances ;*
- *Nuclear structure and nuclear properties ;*
- *Nuclear reactions ;*
- *Radioactive disintegration series ;*
- *Artificial transmutation of elements ;*
- *Nuclear fission and Nuclear fusion ;*
- *Radioisotopes and their uses ;*
- *Carbon dating, synthetic elements.*

It is a well known fact that the atoms contain three fundamental subatomic particles namely : *electrons, protons* and *neutrons.* Protons and neutrons constitute **nucleus** whereas electrons are present in the extranuclear region of the atom. Chemical transformations involve the changes in the valence electrons of the participating atoms while their atomic nuclei remain unaffected. In the beginning of 20th century, another kind of transformation, which involve changes in the atomic nucleus, were observed by the scientists. These transformations are called **nuclear reactions.** The nuclear reactions have become tremendous source of energy all over the world both for peaceful and destructive purposes. The study of nuclear reactions led to the development of a new branch of chemistry called *nuclear chemistry.* The **nuclear chemistry** may, therefore, be defined as ***the branch of chemistry which deals with the study of atomic nucleus and nuclear changes.***

13.1. ATOMIC NUCLEUS AND ITS COMPOSITION

The existence of nucleus in the atom was first of all proposed by E. Rutherford in 1911. Rutherford and his co-workers performed series of scattering experiments and their observations led to the conclusion that entire mass and positive charge is concentrated in a very small region at the centre of the atom, known as **nucleus.** The electrons are revolving around the nucleus in the empty space called *extra nuclear region.*

The size of the nucleus is of the order 10^{-12} to 10^{-13} cm as compared to the size of atoms which is of the order of 10^{-8} cm. In 1932, Chadwick discovered another neutral sub-atomic particle called *neutron.* This led to the conclusion that atomic nucleus is made up of *protons* and *neutrons* and these particles are collectively called **nucleons.** The total number of nucleons is denoted by A and is called **mass number** of the atom.

$$\underset{(A)}{\textit{Mass number}} = \underset{(p)}{\textit{Number of protons}} + \underset{(n)}{\textit{Number of neutrons}}$$

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The nucleus of any atom may be represented by specifying the *atomic number* as a subscript at the left hand bottom of the atomic symbol and the mass number as a superscript at the left hand top of the symbol. For example, the nucleus of most common isotope of carbon is designated as $^{12}_{6}C$.

It may noted that :

(*i*) *Atoms with same number of protons but different number of nucleons are* called **isotopes.**

Some examples are : $^{1}_{1}H$, $^{2}_{2}H$, $^{3}_{1}H$, $^{215}_{84}Po$ and $^{211}_{84}P$

(*ii*) *Atoms with same number of neutrons but different number of nucleons* are called **isotones.**

Some examples are : $^{30}_{14}Si$, $^{31}_{15}P$ and $^{32}_{16}S$

(*iii*) *Atoms with same number of nucleons but different number of protons* are called **isobars.**

Some examples are : $^{40}_{20}Ca$ and $^{40}_{20}Ar$; $^{211}_{82}Pb$ and $^{211}_{83}Bi$.

NUCLEAR DIMENSIONS

(*i*) The radii of various nuclei (assuming them to be spheres) can be calculated from the following empirical relation

$$r = R_0 A^{1/3}$$

where, *r* is the radius of the nucleus A is the mass number and R_0 is constant whose value has been found to be 1.4×10^{-13} cm.

(*ii*) Nuclear dimensions are expressed generally in Fermi units, **1 Fermi = 10^{-13} cm.**

(*iii*) Density of nucleus is very high. It is of the order of 10^{14} g cm^{-3}.

(*iv*) Volume of the nucleus is of the order of 10^{-38} cm^3.

13.2. BINDING ENERGY OF NUCLEUS

As pointed out earlier, the particles present in the nucleus (protons and neutrons) are called **nucleons.** The sum of the individual masses of various particles in the nucleus must be equal to the nuclear mass. But this is not so in actual practice. The nuclear mass is somewhat less than the sum of the individual masses of various nuclear particles. The difference between the actual nuclear mass and the expected nuclear mass (sum of the individual masses of nuclear particles) is referred to as **mass defect.** The *mass defect* can be converted into equivalent energy by means of Einstein equation ($E = mc^2$). *The energy equivalent to mass-defect is responsible for holding the nucleons together and is called* **binding energy of the nucleus.**

For example, let us calculate the binding energy of helium nucleus which contains two protons and two neutrons.

Mass of 2 free neutrons (2 × 1.00867 amu)	= 2.01734 amu
Mass of 2 free protons (2 × 1.00728 amu)	= 2.01456 amu
Sum of the masses of 2 free neutrons and 2 fee protons	= 4.03190 amu
Observed mass of 2 protons and 2 neutrons merged in a helium nucleus	= 4.00150 amu
Mass defect	= 0.03040 amu

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Mass defect in grams $= \frac{0.03040}{6.02 \times 10^{23}}$ g $\left(1 \text{ amu} = \frac{1}{6.02 \times 10^{23}} \text{ g}\right)$

ΔE (Binding energy) $= mc^2$

$$= \frac{0.03040}{6.02 \times 10^{23}} \times (3 \times 10^{10})^2 \text{ ergs}$$

$$= 0.0454 \times 10^{-3} \text{ ergs} = \frac{0.0454 \times 10^{-3}}{1.6 \times 10^{-12}} \text{ eV}$$

$$= 0.0283 \times 10^9 \text{ eV} = 0.0283 \times 10^9 \times 10^{-6} \text{ MeV}$$

$$= \mathbf{28.3 \text{ MeV}}.$$

[*MeV* represents million electron volt also called mega electron volt.]

Thus, binding energy of helium nucleus is 28.3 MeV. The binding energy per nuclear particle (nucleon) is a measure of the stability of nucleus. Binding energy may also be considered as the energy required to separate the individual particles of the nucleus.

It may be noted that binding energy in MeV can be directly found by multiplying the mass defect in amu with (931.48), a coversion factor as explained below :

$$1 \text{ amu} = 1.6603 \times 10^{-27} \text{ kg}$$

$$c = 2.9979 \times 10^8 \text{ ms}^1$$

Using $E = mc^2$

$$= 1.6603 \times 10^{-27} \text{ kg} \times (2.9979 \times 10^8 \text{ ms}^{-1})^2$$

$$= 1.4924 \times 10^{-10} \text{ kg m}^2 \text{ s}^{-2} = 1.4924 \times 10^{-10} \text{ J}$$

$$= \frac{1.4924 \times 10^{-10}}{1.602 \times 10^{-19}} \text{ eV} = 931.48 \times 10^6 \text{ eV} = 931.48 \text{ MeV}$$

Mega electron volt (MeV) $= 1.602 \times 10^{-13}$ *J*

Thus, 1 amu = 931.48 MeV

Energy in MeV = Mass defect (amu) × 931.48.

Mass defect Δm in amu can be directly obtain by using the following formula

$$\Delta m = [Zm_p + (A - Z)\, m_n] - m_N$$

where, Z is atomic number, A is mass number,

m_p mass of proton, m_n mass of neutron,

m_N mass of nucleus $^{A}_{Z}X$.

Packing Fraction. The ratio of the difference between isotopic mass and mass number to its mass number is called packing fraction

$$\textbf{Packing fraction} = \frac{\textbf{Isotopic mass} - \textbf{Mass number}}{\textbf{Mass number}}.$$

Some important facts about packing fraction are :

- Packing fraction is negative or zero for stable nuclei
- Packing fraction is positive for unstable nuclide.
- Quite often packing fraction is multiplied by 10^4 for convenience.

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REVIEW PROBLEMS

13.1. The mass defect of $^{35}_{17}Cl$ is found to be 0.320 amu. Calculate the binding energy per nucleon.

13.2. One mole of a fuel on combustion liberates 1800 kJ of energy. Calculate the loss in mass during the reaction.

13.3. Calculate the binding energy per nucleon in $^{56}_{26}Fe$. The observed mass of Fe atom is 55.9349 amu. Given that mass of electron, proton and neutron as 0.0005486, 1.00728 and 1.00866 amu respectively.

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13.3. NUCLEAR FORCES

The forces which hold nuclear particles together are referred to as **nuclear forces.** The exact nature of these forces is still not clear. However, a Japanese physicst **Yukawa** (1935) has provided theoretical explanation for the origin of these forces. He postulated the presence of a new fundamental particle **meson** (π) in the nucleus of the atom. The meson is approximately 273 times heavier than electron. The meson may be *positively charged* (π^+) or *negatively charged* (π^-) or *neutral* (π°). Yukawa further postulated that in the nucleus, *there is interconversion of proton into neutron* and *vice versa through the exchange of meson.* For example, a proton may change into neutron by losing a positive meson (π^+) or by capture of negative meson (π^-).

$$p \longrightarrow n + \pi^+$$

or

$$p + \pi^- \longrightarrow n$$

Similarly neutron may change into proton either by capture of positive meson (π^+) or by loss of negative meson (π^-)

$$n + \pi^+ \longrightarrow p$$

or

$$n \longrightarrow p + \pi^-$$

The rapid exchange of mesons among the nucleons gives rise to exchange forces which are responsible for holding the nucleons together. Some interesting featurs about nuclear forces are

(*i*) Nuclear forces are about 10^{38} times as strong as gravitational forces and 10^2 times as strong as couloumbic forces.

(*ii*) They are short range forces and are charge independent.

(*iii*) They are not governed by inverse square law.

13.4. RADIOACTIVITY

In 1896, Henri Becquerel was performing experiments which uranium compounds. He accidently placed a crystal of potassium uranyl sulphate [$K_2UO_2(SO_4)_2.2H_2O$] over photographic plate wrapped with usual black paper. On developing the photographic plate, he found the shadow of the crystal on the photographic plate. He repeated this phenomenon a number of times and came to a conclusion that the crystal of potassium uranyl sulphate had emitted some mysterious rays which could penetrate the black paper and had affected the photographic plate. Later on, it was found that thorium compounds also emitted similar rays.

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This phenomenon of spontaneous emission of radiations by an element or its compound was given a name **radioactivity** and the **substances** ***which exhibit this phenomenon*** were called **radioactive substances.** Once discovered, radioactivity become a popular subject for scientific investigations.

Two very popular names associated with the study of radioactivity are *Madam Curie* and her husband *Pierre Curie* who discovered radioactive elements, *polonium, thorium, radium* and *actinium.* Some of these elements possessed radioactive power much larger than uranium. In the later year very large number of radioactive elements have been discovered.

Natural and Induced Radioactivity

Radioactivity can be broadly classified into two categories : *natural radioactivity* and *artificial* or *induced radioactivity.*

(*i*) *If a substance emits radiations by itself, it is said to possess* **natural radioactivity.**

(*ii*) *If a substance does not possess radioactivity* but *starts emitting radiations on exposure to rays from a natural radioactive substance,* it is said to possess **induced radioactivity.**

Nature of Radiations from Radioactive Substances

The nature of the mysterious invisible rays emitted by radioactive substances was determined by Ernest Rutherford. He placed a sample of uranium mineral in a lead box (Fig. 13.1). The lead absorbed all other radiations except those which pass through the slit to constitute the beam. The radiations emitted by the uranium mineral could be resolved into three types by the application of electrical field.

(*a*) The rays which deflected slightly towards –ve electrode were named as ***alpha*** (α) ***rays.***

(*b*) The rays which deflected towards +ve electrode were named as ***beta*** (β) ***rays.***

(*c*) The rays which remained undeflected were named as ***gamma*** (γ) ***rays.***

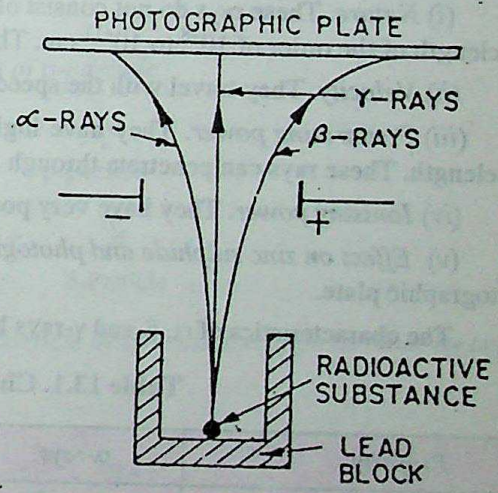

Fig. 13.1. Behaviour of α, β and γ-rays in electrical field.

Later on, it was established that these three types of radiations were given off from all radioactive substances. Let us study the properties of these three types of radiations.

(*a*) **Alpha (α) Rays**

(*i*) *Nature.* The study of α-rays in electrical and magnetic field has shown that these rays consist of material particles carrying 2 units of positive charge and a mass equal to 4 amu. In other words, α-particles are helium nuclei [He^{2+}].

(*ii*) *Velocity.* They are shot out with a velocity about 1/10th of the velocity of light.

In fact, the actual speed of α-particles depends upon the nature of substance from which they are ejected. Energy range of α-particles is 4.9 MeV.

(*iii*) *Penetrating power.* They do not possess high penetrating power because of their large mass. They can penetrate through a mica sheet, a thin metal foil or through a few centimetres in air. They can penetrate through a sheet of aluminium up to a thickness of 0.02 cm.

(*iv*) *Ionising power.* α-particles can ionise the gas through which they pass. This is because of the fact that they knock off electrons from neutral gas molecules on colliding with them resulting in the ionisation of gas.

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(*v*) *Effect on zinc sulphide.* Due to the high kinetic energy, they produce luminosity when they strike zinc sulphide plate.

(*vi*) *Effect on photographic plate.* α-particles also affect the photographic plate.

(*b*) **Beta (β) Rays**

(*i*) *Nature.* β-rays have been found to consist of particles having same charge and mass as electrons. Their *e/m* ratio is some as that of electrons. These particles are designated as $_{-1}^{0}e$ or $_{-1}^{0}\beta$.

(*ii*) *Velocity.* β-particles move much faster in comparison to α-particles. They travel with the speed almost approaching the speed of light. Energy range is 0.5 to 2 MeV.

(*iii*) *Penetrating power.* β-particles have far more penetrating power due to small mass and high velocity. They can penetrate through a sheet of aluminium having thickness upto 0.2 cm.

(*iv*) *Ionising power.* β-rays have poor ionising power inspite of their high speed. It is because of the fact that they possess low kinetic energy due to their extremely small mass.

(*v*) *Effect on zinc sulphide and photographic plate.* β-particles have very little effect on zinc sulphide due to their low kinetic energy. However, their photographic activity is greater than that of α-particles.

(*c*) **Gamma (γ) Rays**

(*i*) *Nature.* These rays do not consist of material particles but they are electromagnetic waves having wavelength of the order of 10^{-8} to 10^{-11} cm. They are electrically neutral.

(*ii*) *Velocity.* They travel with the speed of light. Their energy range is 0.1 – 2 MeV.

(*iii*) *Penetrating power.* They have high penetrating power because of their high velocity and small wavelength. These rays can penetrate through a sheet of aluminium having thickness upto 100 cm.

(*iv*) *Ionising power.* They have very poor ionising power because of their non-material nature.

(*v*) *Effect on zinc sulphide and photographic plate.* The produce very little effect on zinc sulphide or photographic plate.

The characteristics of α, β and γ-rays have been summed up in Table 13.1.

Table 13.1. Characteristics of α, β and γ-rays

	Property	*α-rays*	*β-rays*	*γ-rays*
1.	Mass	6.67×10^{-27} kg or 4 amu.	9.11×10^{-31} kg	Negligible
2.	Charge	+ 2 units	– 1 units	0
3.	Identity	Helium nuclei (He^{2+})	Electrons	High energy radiations
4.	Velocity	Nearly $\frac{1}{10}$th that of light	Nearly same as that of light	Same as that of light
5.	Effect of electric and magnetic fields	Deflected towards negative pole	Deflected towards positive pole	Not deflected
6.	Penetrating power	Small	Large, 100 times that of α-rays	Very large, 10000 times that of α-rays
7.	Effect on photographic plate and zinc sulphide	Affected more strongly than by β and γ-rays	Effect is less than α-rays	Least effect

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Cause of Radioactivity

It has been found that the stability of nucleus depends upon its *neutron to proton (n/p) ratio.* If we plot the number of neutrons (*n*) vs. number of protons (*p*) for nuclei of various elements as shown in Fig. 13.2, we find that :

(*i*) *light nuclei (A < 20) have n/p ratio close to unity*

(*ii*) *for heavy nuclei (A > 20) the n/p ratio increases progressively due to dominance of number of neutrons.* It is evident that most of the stable nuclei (non-radioactive) have *n/p* ratio between **1 – 1.6.** These nuclei lie in the shaded region of the plot which is also called ***stability belt*** or ***stability zone.***

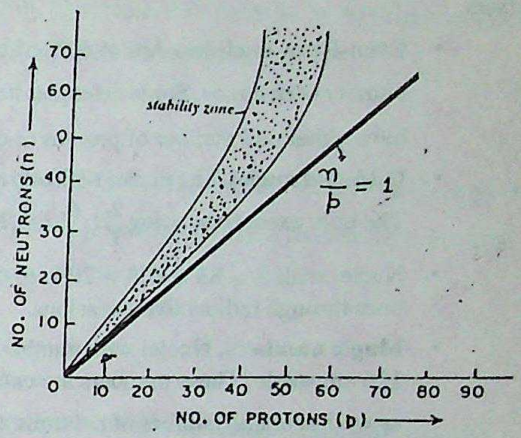

Fig. 13.2. *n/p* ratio for stable nuclei.

However, the elements whose nuclei do not fall within the stability limit are said to be unstable. The unstable nuclei, whose *n/p* ratio is either less than 1 or greater than 1.6, disintegrate giving out α, β or γ-rays in their attempt to attain stability. The process of disintegration continues till the *n/p* ratio falls within the stability limit.

For example,

(*i*) *n/p ratio decreases, in general, by the emission of* β*-particle*

$$\underset{(n/p = 1.33)}{{}^{14}_{6}C} \longrightarrow \underset{(n/p = 1)}{{}^{14}_{7}N} + \underset{\beta\text{-particle}}{{}^{0}_{-1}e}$$

$$\underset{(n/p = 1.23)}{{}^{29}_{13}Al} \longrightarrow \underset{(n/p = 1.07)}{{}^{29}_{14}Si} + \underset{\beta\text{-Particle}}{{}^{0}_{-1}e}$$

(*ii*) *n/p ratio increases either by the emission of* α*-particle or by emission of positron or by capture of orbital (k-electron) electron.*

(*a*) α-*Decay*

$$\underset{(n/p = 1.5)}{{}^{238}_{92}U} \longrightarrow \underset{(n/p = 1.6)}{{}^{234}_{90}U} + \underset{\alpha\text{-Particle}}{{}^{4}_{2}He}$$

(*b*) ***Positron emission***

$$\underset{(n/p = 0.83)}{{}^{11}_{4}C} \longrightarrow \underset{(n/p = 1.2)}{{}^{11}_{5}B} + \underset{\text{Positron}}{{}^{0}_{+1}e}$$

(*c*) ***Capture of K-electron.*** This process is not very common and occurs in case of nuclei with low *n/p* ratio and having insufficient energy for positron emission. Here, the nucleus may capture electron from K-shall (closest to nucleus) and converts a proton into neutron with the release of nutrino.

$$\underset{(n/p = 0.75)}{{}^{7}_{4}Be} + \underset{(k\text{-electron})}{{}^{0}_{-1}e} \longrightarrow \underset{(n/p = 1.33)}{{}^{7}_{3}Li} + \underset{\text{nutrino}}{\nu}$$

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Some significant facts About Stable nuclei. A study of stable nuclei have revealed the following interesting facts.

- **Even-Even nuclides.** About 60% of the stable nuclei have both even number of protons and even number of neutrons. Some examples being $^{12}_{6}C$, $^{16}_{8}O$, $^{40}_{20}Co$. etc. Almost all the remaining stable nuclei have either odd number of protons or odd number of neutrons.
- **Odd-odd nuclei.** The nuclei with odd number of protons and odd number of neutrons are least stable. The only exception, being $^{2}_{1}H$, $^{6}_{3}Li$, $^{10}_{5}Be$, $^{14}_{7}N$, $^{180}_{73}Ta$.
- Nuclei with Z > 83 and A > 209 are unstable and spontaneously transforms themselves into lighter ones through radioactive emissions.
- **Magic numbers.** Nuclei with number of neutrons or numbers of protons equal to 2, 8, 20, 50, 82 or 126 are stable. These numbers are called ***magic numbers.*** The nuclei with magic number of protons as well as magic number of neutrons are most stable. Some examples being, $^{4}_{2}He$, $^{16}_{8}O$, $^{40}_{20}Ca$, $^{208}_{82}Pb$.

13.5. NUCLEAR CHANGES AND GROUP DISPLACEMENT LAW

It has been pointed out earlier that radioactive element emits, α, β and γ-rays. The emission of α and β-rays bring some changes in the nucleus of the atom and the new element formed as a result of these changes is called **daughter element.**

The equations representing the nuclear changes are called **nuclear chemical equations.** In writing the nuclear chemical equation, the following points must be kept in mind :

(*i*) *Sum of the mass numbers of various reactant species must be equal to the sum of the mass numbers of the product species.*

(*ii*) *Sum of the charge numbers (atomic numbers) of reactant species and that of the product species must be equal.*

The notations of some of the species that participate in nuclear reactions are given below in tabular form.

Species	*Notation*
α-particle	$^{4}_{2}He$
Proton	$^{1}_{1}H$
Deutron	$^{2}_{1}H$
Neutron	$^{1}_{0}n$
Electron or β-particle	$^{0}_{-1}e$ or β^-
Positron	$^{0}_{+1}e$ or β^+

Let us now proceed to discuss the changes produced by α, β and γ emission.

1. Emission of α-rays. When a nucleus emits an α-particle ($^{4}_{2}He$) its *atomic number* is reduced by *two units* and its *mass number* is reduced by *four units.* The daughter element, thus, formed occupies a position in

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the periodic table *two places left* of the parent element. For example, emission of α-particle from uranium-238 ($^{238}_{92}U$) produces a thorium nucleus ($^{234}_{90}Th$). The above nuclear change can be represented as :

$$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He.$$

2. **Emission of β-rays.** The β-particles are electrons ($^{0}_{-1}e$) with mass number zero and charge equal to – 1. Since nucleus does not contain electrons. Therefore, emission of β-particle from a radioactive nucleus is believed to arise from the coversion of a neutron ($^{1}_{0}n$) into proton and electron.

$$\underset{\text{Neutron}}{^{1}_{0}n} \longrightarrow \underset{\text{Proton}}{^{1}_{1}H} + \underset{\text{Electron}}{^{0}_{-1}e}$$

When, there is an emission of β-particle, the proton is retained by the nucleus. Thus, the daughter element so formed has atomic number one more than the parent element. However, there is no change in its mass number. Thus, the daughter element occupies a position in the periodic table *one place right* to the parent element. For example, thorium ($^{234}_{90}Th$) gives protactinium ($^{234}_{91}Pa$) by the emission of β-particle. It may be represented as

$$\underset{\text{Thorium}}{^{234}_{90}Th} \longrightarrow \underset{\text{Protactinium}}{^{234}_{91}Pa} + {}^{0}_{-1}e$$

Similarly,

$$\underset{\text{Carbon}}{^{14}_{6}C} \longrightarrow \underset{\text{Nitrogen}}{^{14}_{7}N} + {}^{0}_{-1}e$$

The emission of γ-*rays* does not produce any change either in the mass number or in the atomic number of the nucleus. Emission of γ-rays is virtually observed in all nuclear reactions from the nuclei which are left in excited state by an earlier emission of α or β-particle and it causes the decrease in the energy of the nuclide.

Group Displacement Law

Soddy and Fazan have summed up the emission of α and β-particles in the form of the law known as *Group Displacement Law.* The law is stated as follows :

The emission of α-particle by an element results in the formation of new element which lies two places left to the parent element and the emission of β-particle results in the formation of a new element which lies one place right to the parent element in the periodic table.

For example, ***thorium*** ($^{234}_{90}Th$) formed by emission of α-particle from ***Uranium-238*** ($^{238}_{92}Pa$) lies two places left of Uranium, and emission of β-particle from ***thorium*** results in the formation of ***protactinium*** ($^{234}_{91}Pa$) which lies one place right of the thorium.

Formation of isobars, isotopes and isodiaphers

(*i*) During radioactive emissions, the emission of **β-particle** results in the formation of **isobar** of the parent element.

(*ii*) The emission of **α-particle** results in the formation of **isodiapher** of the parent element.

Isodiaphers *are, in fact, the species which have same* **isotopic number (N – Z) or (A – 2Z).**

For example, $^{19}_{9}F$ *and* $^{39}_{19}K$ *have same value of isotopic number (1).*

(*iii*) The emission of **α-particle** followed by emission of **two β-particles** produces **isotope** of the parent element.

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This is illustrated by the example given below :

$$^{215}_{84}\text{Po} \xrightarrow{-\alpha} {}^{211}_{82}\text{Pb} \xrightarrow{-\beta} {}^{211}_{83}\text{Bi} \xrightarrow{-\beta} {}^{211}_{84}\text{Po}$$

Group → **16** **14** **15** **16**

Here, $^{211}_{82}$Pb and $^{211}_{82}$B$_1$ are **isobars.**

$^{215}_{84}$Po and $^{211}_{82}$Pb are **isodiaphers.**

$^{215}_{84}$P$_0$ and $^{211}_{84}$P$_0$ are **isotopes.**

Example 13.1. *$^{238}_{92}U$ emits one α-particle followed by the emission of two β-particles as shown*

$$^{238}_{92}U \xrightarrow{-\alpha} X \xrightarrow{-\beta} Y \xrightarrow{-\beta} Z$$

Label the above elements in the consecutive nuclear reactions.

Solution. Indicating the atomic numbers and mass number of various elements, we have

$$^{238}_{92}\text{U} \xrightarrow{-\alpha} {}^{234}_{90}\text{X} \xrightarrow{-\beta} {}^{234}_{91}\text{Y} \xrightarrow{-\beta} {}^{234}_{92}\text{Z}$$

Thus, we find mass number of Z is 234 while atomic numbers is 92. Thus, Z is an **isotope** of $^{238}_{92}$U.

Thus, **X is $^{238}_{90}$Th ; Y is $^{234}_{91}$Pa and Z is $^{234}_{92}$U.**

Example 13.2. *How many α and β-particles are emitted in passing down from $^{232}_{90}Th$ to $^{208}_{82}Pb$?*

[I.I.T. 1988 ; CBSE (2) 1992]

Solution. Let the number of α-particles emitted be x and β-particles be y. The net nuclear reaction can be represented as :

$$^{232}_{90}\text{Th} \longrightarrow {}^{208}_{82}\text{Pb} + x\,{}^{4}_{2}\text{He} + y\,{}^{0}_{-1}e \qquad ...(i)$$

Balancing the mass numbers (A) on both the sides of the above equation (*i*)

$$232 = 208 + 4x + 0 \times y$$

or $$= 208 + 4x$$

or $$x = \frac{232 - 208}{4} = \frac{24}{4} = 6$$

Thus, the number of α-particles emitted = 6.

Now balance the atomic number on both sides of the equation (*i*)

$$90 = 82 + 2x + y(-1) = 82 + 2 \times 6 - y$$

$$= 82 + 12 - y$$

or $$y = 82 + 12 - 90 = 4$$

Thus, the number of β-particles emitted = 4.

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THE QUARK MODEL

Neutrons and Protons have been considered to be fundamental building blocks of the nucleus since long. However, the recent research have led scientist to achieve break-through in this field. It has been established that the nucleons are further made of particles called **Quarks**. The various quarks along with their symbols, charges and masses are given below :

Particle name	*Symbol*	*Charge x (electronic charge)*	*Mass y(electronic mass)*
Up quark	*u*	+ 2/3	10
Down quark	*d*	– 1/3	20
Strange quark	*s*	– 1/3	200
Charm quark	*c*	+ 2/3	3,000
Bottom quark	*b*	– 1/3	9,000
Top quark	*t*	+ 2/3	60,000

Studies have revealed the following composition for neutron and proton in terms of quarks. **Proton** is made of *two up quarks* and *one down quark* whereas **neutron** is made of *two down quarks* and *one up quark*

Nucleon	**Constituent quarks**	**Charges**	**Net charge**
Proton (p)	$u + u + d$	$(+2/3) + (+2/3) + (-1/3)$	*+ 1*
Neutron (n)	$u + d + d$	$(+2/3) + (-1/3) + (-1/3)$	*0*

The quark model not only helps us to understand the nucleus but also provides a better understanding about the interaction of nuclear particles as well as nuclear processes. For example, β-*decay* has been postulated earlier, as conversation of neutron into proton (*p*), electron ($\bar{e}$) and anti-nutrino ($\bar{\gamma}$)

$$n \longrightarrow p + \bar{e} + \bar{\gamma}$$

In terms of quarks, the β-decay is supposed to occur by changing a *down quark* (*d*) into up quark (*u*) and *electron*

$$n\,(udd) \longrightarrow p\,(uud) + \bar{e} + \bar{\gamma}.$$

REVIEW PROBLEMS

13.4. After emitting a series of α and β-particles $^{238}_{92}U$ changes to $^{206}_{82}Pb$. Calculate the number of α and β-particles emitted.

13.5. How many α and β-particles are emitted when $^{238}_{92}U$ changes to $^{226}_{88}Ra$?

13.6. Calculate the mass number, atomic number and group in the periodic table for Bi in the following disintegration sequence.

$$^{226}_{88}Ra \xrightarrow{-\alpha} Rn \xrightarrow{-\alpha} Po \xrightarrow{-\alpha} Pb \xrightarrow{-\beta} Bi.$$

Also predict as to which of them are isodiaphers or isobars.

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13.6. RADIOACTIVE DISINTEGRATION SERIES

We have already learnt that the emission of α or β-particles from a radioactive element results in the formation of new element called **daughter element.** If the daughter element still has unstable nucleus, it further disintegrates by emitting α or β-particle and produces a new daughter element. This process of successive disintegration continues till the *end product,* is an element with stable nucleus. *The series of spontaneous changes that take place starting from a radioactive element till the formation of a non-radioactive end product is called* **radioactive disintegration series.**

One of the natural radioactive series, which was first to be discovered is *uranium-238* series. It involves *fourteen* separate steps, *eight* of which involve α-emission whereas *six* involve β-emission. The various steps have been summarized in Table 13.2. The overall process can be written as

$$^{238}_{92}U \longrightarrow {}^{206}_{82}Pb + 8\,{}^{4}_{2}He + 6\,{}^{0}_{-1}e$$

Besides uranium-238 series, the other natural radioactive series are :

thorium series, actinium series and neptunium series.

It may be noted that in natural radioactive series, the changes in mass numbers are produced by the emission of α-particles only because emission of β-particles do not bring about any change in mass number.

Table 13.2. Radioactive Disintegration Series of $^{238}_{92}U$

Symbol	*Name of isotope*	*Half-life period*
$^{238}_{92}U$	Uranium-238	4.51×10^9 years
↓ − α		
$^{234}_{90}Th$	Thorium-234	24.1 days
↓ − β		
$^{234}_{91}Pa$	Protactinium-234	1.18 minutes
↓ − β		
$^{234}_{92}U$	Uranium-234	2.48×10^5 years
↓ − α		
$^{230}_{90}Th$	Thorium-230	8.0×10^4 years
↓ − α		
$^{226}_{88}Ra$	Radium-226	1.62×10^3 years
↓ − α		
$^{222}_{86}Rn$	Radon-222	3.82 days
↓ − α		
$^{218}_{84}Po$	Polonium-218	3.05 minutes
↓ − α		
$^{214}_{82}Pb$	Lead-214	26.8 minutes
↓ − β		
$^{214}_{83}Bi$	Bismuth-214	19.7 minutes
↓ − β		

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Symbol	*Name of isotope*	*Half-life period*
$^{214}_{84}Po$	Polonium-214	1.64×10^{-4} seconds
$\downarrow -\alpha$		
$^{210}_{82}Pb$	Lead-210	19.4 years
$\downarrow -\beta$		
$^{210}_{83}Bi$	Bismuth-210	5.0 days
$\downarrow -\beta$		
$^{210}_{84}Po$	Polonium-210	138.4 days
$\downarrow -\alpha$		
$^{206}_{82}Pb$	Lead-206	STABLE

Since α-particle has a mass number equal to 4 units, hence, change in mass number of parent and daughter nuclide will always occur by 4 units. For example, if we divide the mass number of uranium (238) by 4, it gives a remainder equal to 2. Now mass number of each nuclide of uranium series will give a remainder equal to 2 when divided by four. It means that mass numbers of various nuclide of uranium series can be represented by formula $(4n + 2)$ when n is an integer. This helps us to classify various radioactive series in terms of the general formulae of the mass numbers of various nuclides involved. These are :

(*i*) **4n-Series.** This is also called **thorium series.** It starts from $^{232}_{90}Th$ and ends with $^{208}_{82}Pb$. Mass number of each nuclide of the series is divisible by 4.

(*ii*) **(4n + 1) Series.** This is also called **neptunium series.** It starts from $^{237}_{93}Np$ and ends with $^{209}_{83}Bi$. Mass number of each nuclide of the series gives a remainder equal to 1 when divided by 4.

(*iii*) **(4n + 2) Series.** This is also called **Uranium series.** It starts from $^{238}_{92}U$ and ends with $^{206}_{82}Pb$. Mass number of each nuclide of the series gives a remainder of 2 when divided by 4.

(*iv*) **(4n + 3) Series.** This is also called **actinium series.** It starts from $^{235}_{92}U$ and ends with $^{207}_{82}Pb$. Mass number of each nuclide of series gives a remainder of 3 when divided by 4.

The various series along with the values of n fro *initial* and *last elements* are given in Table 13.3.

Table 13.3. Various Radioactive Series

Series	*Name of series*	*Initial nuclide*	*Last stable nuclide*	*n for initial element*	*n for last element*
4n	Thorium series	$^{232}_{90}Th$	$^{208}_{82}Pb$	58	52
4n + 1	Neptunium series	$^{237}_{93}Np$	$^{209}_{83}Bi$	59	52
4n + 2	Uranium series	$^{238}_{92}U$	$^{206}_{82}Pb$	59	51
4n + 3	Actinium series	$^{235}_{92}U$	$^{207}_{82}Pb$	58	51

*A nucleus of a given mass number and atomic number produced in a nuclear reaction is referred to as **nuclide.** For examples $^{234}_{90}Th$ is called *thorium-234 nuclide.*

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13.7. RATE OF NUCLEAR DISINTEGRATION

The activity of a radioactive element is measured by the rate at which it changes into its daughter element. The rate of radioactive disintegration is *independent of temperature, pressure or the state of chemical combination of the element.* However, it does depend upon the nature of the element. The rate of nuclear disintegration of radioactive substance is determined by counting the number of particles emitted per unit time by using instruments like *Scintillation Counter,* or *Geiger-Muller Counter or Wilson cloud chamber.*

It has been experimentally observed that in all nuclear disintegration reactions the *rate of disintegration (or decay) is directly proportional to the number of atoms present in a sample at that time.* Since it refers to the characteristic of a first order reaction. Therefore, radioactive disintegration can be regarded as similar to first order chemical reaction. Consider a radioactive element A disintegrating to give products.

$$A \longrightarrow \text{Products}$$

Let N_0 be the number of atoms in the beginning at time $t = 0$

N be the number of atoms of A at time 't'.

The rate of disintegration *i.e.*, $\frac{-dN}{dt}$ at time 't' is directly proportional to N. It can be expressed as

$$\frac{-dN}{dt} \propto N$$

or

$$\frac{-dN}{dt} = \lambda N \qquad ...(13.1)$$

where λ is called *decay constant* or *disintegration constant.*

Rearrange equation (13.1) and integrate it

$$-\int \frac{dN}{N} = \int \lambda \, dt$$

or

$$-\ln N = \lambda t + C \qquad ...(13.2)$$

where C is constant of integration.

Now, when $t = 0$, number of atoms = N_0

$$\therefore \quad -\ln N_0 = 0 + C \text{ or } C = -\ln N_0$$

Substitute the value of C is equation (13.2),

$$-\ln N = \lambda t - \ln N_0$$

or

$$\ln N_0 - \ln N = \lambda t$$

or

$$\ln \frac{N_0}{N} = \lambda t$$

Converting natural logarithm to logarithm to base 10, we have

$$2.303 \log \frac{N_0}{N} = \lambda t$$

or

$$\log \frac{N_0}{N} = \frac{\lambda t}{2.303}$$

or

$$\boxed{\lambda = \frac{2.303}{t} \log \frac{N_0}{N}} \qquad ...(13.3)$$

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Half-Life Period

The time required for the decay of the radioactive element to one-half of its original amount is called **half life period.** This is usually denoted by $t_{1/2}$. Each radioactive element has its characteristic half-life period. For example, the half-life for the radioactive decay of *uranium-238* is 4.51×10^9 years and that of *radium-226* is 1.62×10^3 years.

The half-life period ($t_{1/2}$) does not depend upon the initial amount of radioactive element but it depends upon the value of λ. This can be proved as follows :

After time $t_{1/2}$, half of the atoms of radioactive substance disintegrate, so that $N = \frac{N_0}{2}$.

Substituting in equation (13.3), we have

$$\log \frac{N_0}{N_0/2} = \frac{\lambda t_{1/2}}{2.303}$$

or

$$t_{1/2} = \frac{2.303}{\lambda} \times \log 2$$

or

$$\boxed{t_{1/2} = \frac{0.693}{\lambda}} \qquad (\log 2 = 0.3010)$$

Since λ is a constant, *the time required for disintegration of one-half of the original amount of radioactive substance is independent of the initial amount of radioactive substance.*

Average life period. The reciprocal of decay constant is called average life period. It is generally denoted by τ (*tau*)

$$\tau = 1/\lambda$$

Relationship between half life **period and average life period**

Half life period $t_{1/2}$ is given by

$$t_{1/2} = \frac{0.693}{\lambda} = 0.693\, t$$

or

$$\tau = t_{1/2}/0.693 = 1.44\, t_{1/2}$$

∴ Average life period = 1.44 × Half-life period.

Significance of Half-Life Period

(*i*) **Stability of nuclei.** ***The value of half life period can give some idea regarding the relative stability of radio-isotopes.*** An isotope having longer half-life period is relatively more stable than the isotope with shorter half-life period. For example, ^{238}U has a longer half-life period (4.5×10^9 years) whereas ^{214}Po has a very short half-life period (1.64×10^{-8} seconds). It implies that ^{214}Po is highly unstable whereas ^{238}U is quite stable as far as radioactive decay is concerned.

(*ii*) *Half life period is independent of initial amount of radioactive substance.*

(*iii*) *The amount of substance left after n half lives is given by*

$$N = N_0(1/2)^n$$

where, N is amount after *n* half lives

N_0 is the initial amount of radioactive substance.

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Units of Radioactivity. The SI unit of radioactivity is, *Bacqueral* (**Bq**) which is defined as *one disintegration per second.* Earlier, radioactivity was expressed in terms of *curies* (C_i). **One curie** refers to the activity of one gram of radium, and is equal to 3.7×10^{10} *disintegrations per second.*

$$1C_i = 3.7 \times 10^{10} \text{ disintegrations per second}$$

$$\therefore \quad \mathbf{1C_i = 3.7 \times 10^{10} \text{ Bq}}.$$

Example 13.3. *The half-life period of a certain radioactive element is 100 seconds. Calculate the disintegration constant. Also calculate the time during which 1 g of the element is reduced to 0.01 g.*

Solution. For radioactive decay,

$$t_{1/2} = \frac{0.693}{\lambda}$$

$$\therefore \quad \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{100} = \mathbf{6.93 \times 10^{-3} \text{ sec}^{-1}}$$

Now
$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N}$$

Here,
$$\frac{N_0}{N} = \frac{1}{0.01} = 100$$

$$\therefore \quad t = \frac{2.303}{6.93 \times 10^{-3}} \log 100$$

$$= \frac{2.303}{6.93} \times 10^3 \log 100 = \frac{2.303}{6.93} \times 2 = 664.64 \text{ sec} = \mathbf{11.08 \text{ min.}}$$

REVIEW PROBLEMS

13.7. Radioactive carbon in wood decays with a half-life of 5770 years. What is the rate constant (in year^{-1}) for the decay ? What fraction would remain after 11540 years ?

13.8. A radioactive element decays at such a rate that after 68 minutes only one-fourth of its original amount remains. Calculate disintegration constant and half-life period.

13.9. The half-life of Hg-203 is 49.6 days. How much of 0.200 mg sample of Hg-203 will remain after 6 months ?

13.10. A radioactive isotope has a half-life of 20 days. What amount of isotope is left after 40 days if the original amount is 5 g ?

13.11. A radioactive isotope decays at such a rate that after 100 minutes only one-eighth of the original amount remains. Calculate $t_{1/2}$ and λ.

13.12. Starting with 1 g of radioactive sample, 0.25 g is left after 20 days. Calculate the rate constant λ for the decays of radioisotope. *[CBSE 1992]*

13.13. Starting with 1.0 g of a radioactive sample, 0.25 g of it is left after 5 days. Calculate the amount which was left after a day. *(A.I. CBSE 1993)*

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13.8. ARTIFICIAL TRANSMUTATION OF ELEMENTS

The emission of α or a β-particle from the radioactive element results in the formation of a new element. This urged scientists to find methods for the conversion of naturally stable elements into other elements by

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artificial disintegration. The artificial disintegration could be caused by bombarding the nuclei of the atoms with high speed sub-atomic particles such as α-*particles*, β-*particles, neutrons, protons and deutrons, etc.* ***This process of conversion of one element into the other by artificial means, i.e. by bombarding the nuclei of atoms with high speed sub-atomic particles is called artificial transmutation of elements.***

The first artificial transmutation experiment was reported by Rutherford in 1919, in which a nitrogen-14 nuclide was bombarded by α-particle to get oxygen-17 nuclide.

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H \quad ...(i)$$

The sub-atomic particles used for bombarding the target nuclei are called **bombarding particles** or **projectiles.** Before bombarding the *target nuclei*, the bombarding projectiles are imparted high energy by the device called **particle accelerator.** The various particle accelerators are : *linear accelerator, cyclotron* and *synchroton, etc.* The process of conversion of one nuclide into another is also referred to as **nuclear reaction,** which in general, can be expressed as

Target nuclide + *Bombarding projectile* ⟶ *New nuclide* + *Ejected particle*

Representation of Nuclear Reactions

For the sake of brevity, the nature of nuclear reaction is represented by writing the *bombarding projectile* and *ejected particle* within brackets. For example, the nuclear reaction represented by equation (*i*) can be termed as (α, *p*) *reaction* because here, α-particle is a bombarding projectile and proton is the ejected particle. The same can be briefly represented as

$$^{14}_{7}N\ (\alpha, p)\ ^{17}_{8}O.$$

It may be noted that out of various bombarding particles the *neutrons* are particularly useful because they do not carry any charge. On the other hand, the *protons, deutrons* and α-*particles* are positively charged particles and are repelled by the target nuclei. Let us now study some examples of various types of nuclear reactions.

(*i*) *Transmutation by* α-*particles* ($^{4}_{2}He$)

$$^{9}_{4}Be + ^{4}_{2}He \longrightarrow ^{12}_{6}C + ^{1}_{0}n \quad (\alpha, n)\ type$$

$$^{19}_{9}F + ^{4}_{2}He \longrightarrow ^{22}_{10}Ne + ^{1}_{1}H \quad (\alpha, p)\ type$$

(*ii*) *Transmutation by proton* ($^{1}_{1}H$)

$$^{31}_{15}P + ^{1}_{1}H \longrightarrow ^{31}_{16}S + ^{1}_{0}n \quad (p, n)\ type$$

$$^{12}_{6}C + ^{1}_{1}H \longrightarrow ^{13}_{7}N + \gamma\text{-rays} \quad (p, r)\ type$$

$$^{9}_{4}Be + ^{1}_{1}H \longrightarrow ^{8}_{4}Be + ^{2}_{1}H \quad (p, d)\ type$$

(*iii*) *Transmutation by neutrons* ($^{1}_{0}n$)

$$^{27}_{13}Al + ^{1}_{0}n \longrightarrow ^{27}_{12}Mg + ^{1}_{1}H \quad (n, p)\ type$$

$$^{16}_{8}O + ^{1}_{0}n \longrightarrow ^{13}_{6}C + ^{4}_{2}He \quad (n, \alpha)\ type$$

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(*iv*) *Transmutation by deutrons* (^2_1D *or* ^2_1H)

$$^6_3Li + ^2_1H \longrightarrow ^7_3Li + ^1_1H \qquad (d, p) \text{ type}$$

$$^{75}_{32}As + ^2_1H \longrightarrow ^{76}_{32}As + ^1_1H \qquad (d, p) \text{ type}$$

(*v*) *Transmutation by* γ*-radiations*

Some of the cases of transmutation by γ-radiations have also been reported.

$$^9_4Be + \gamma \longrightarrow ^8_4Be + ^1_0n \qquad (\gamma, n) \text{ type}$$

In the above nuclear equations the letters used to express the type of the reaction represent :

α for ^4_2He ; *p* for *proton* ; *n* for *neutron*

d for *deutron* ; γ for γ*-radiations*

Various Categories of Nuclear Reactions :

The nuclear reactions in general can be classified into various types.

1. Projectile capture particle emission. This type of reactions involve the emission of another elementary particle along with the product. Majority of nuclear reactions fall in this category.

$$^{23}_{11}Na + \underset{\text{Projectile}}{^4_2He} \longrightarrow ^{26}_{12}Mg + \underset{\text{Particle}}{^1_1H}$$

2. Projectile capture reactions. In there reactions the bombarding particle is absorbed with or without the emission of γ-radiations.

$$^{27}_{13}Al + ^1_0n \longrightarrow ^{28}_{13}Al + \gamma$$

3. Spallation reactions. In these reactions, the high speed projectiles (Energy approx. 40 MeV) chip out fragments from the heavy target nuclide.

$$^{63}_{29}Cu + ^4_2He \longrightarrow ^{34}_{17}Cl + 14\,^1_1H + 16\,^1_0n$$

4. Nuclear Fission. In these reactions a heavy nucleus is broken down into two or more medium heavy fragments along with the liberation of large amount of energy.

$$^{235}_{92}U + ^1_0n \longrightarrow ^{141}_{56}Ba + ^{92}_{36}Kr + 3\,^1_0n + 2000 \text{ MeV}$$

5. Fusion reactions. These reactions involve fusion of two light nuclei to produce a heavy nuclide along with large amount of energy

$$^2_1H + ^3_1H \longrightarrow ^4_2He + ^1_0n + 17.6 \text{ MeV}$$

Difference between Chemical Reactions and Nuclear Reactions

Some important differences between the chemical reactions and nuclear reactions are given below in tabular form.

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Nuclear Reactions	*Chemical Reactions*
1. No breaking or making of bonds is involved.	1. They generally involve breaking of old bonds and formation of new chemical bonds.
2. Generally proceed with tremendous release of energy.	2. They may involve evolution of absorption of energy.
3. Temperature and pressure do not affect their rates.	3. Their rates of reaction are affected by temperature and pressure conditions.
4. Such reactions are generally irreversible.	4. They can be reversible as well as irreversible.
5. They involve the conversion of one nuclide into the other.	5. They simply involve the rearrangement of atoms and donot involve any change in the nucleus.

REVIEW PROBLEMS

13.14. Predict the bombarding projectile in each of the following cases :

(*i*) $^{209}_{83}Bi + ? \longrightarrow ^{210}_{84}Po + ^{1}_{0}n$ (*ii*) $^{2}_{1}H + ? \longrightarrow ^{1}_{1}H + ^{1}_{0}n$

(*iii*) $^{82}_{34}Se + ? \longrightarrow ^{83}_{34}Se + \gamma\text{-ray}$ (*iv*) $^{27}_{13}Al + ? \longrightarrow ^{28}_{14}Si + ^{1}_{0}n$.

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Artificial or Induced Radioactivity

It has been observed that artificial transmutation of elements quite often results in the formation a radioactive product although its half-life period is very small. The first such observation was made by *Irene Curie* and her husband *F. Joliot* in 1934. They found that when *aluminium, magnesium*, and *boron* were bombarded with α-particles, the products formed were radioactive which disintegrated spontaneously with the emission of **positron** which has the same mass as that of electron but opposite charge, *i.e.*, positively changed electron ($^{0}_{+1}e$).

The above changes have been represented in the tabular form.

Parent stable Element	*Mode of Transmutation*	*Radioactive isotope*	*Emission of positron*
$^{27}_{13}Al$	$\xrightarrow[-^{1}_{0}n]{+^{4}_{2}He}$	[$^{30}_{15}P$]	$\longrightarrow ^{30}_{14}Si + ^{0}_{+1}e$
$^{24}_{12}Mg$	$\xrightarrow[-^{1}_{0}n]{+^{4}_{2}He}$	[$^{27}_{14}Si$]	$\longrightarrow ^{27}_{13}Al + ^{0}_{+1}e$
$^{10}_{5}B$	$\xrightarrow[-^{1}_{0}n]{+^{4}_{2}He}$	[$^{13}_{7}N$]	$\longrightarrow ^{13}_{6}C + ^{0}_{+1}e$

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Such a phenomenon in which *artificial transmutation of a stable nucleus leads to the formation of radioactive isotope* is called **artificial radioactivity** or **induced radioactivity.**

It may be noted that the radioactive isotopes formed by artificial transmutation usually have very short half-life periods. Consequently, they are rarely found in nature. They decay off as soon as they are formed. The artificial isotopes not only lose positrons but also disintegrate by losing β-particles or other particles as well. For example,

$$\underset{\text{Stable nucleus}}{{}^{23}_{11}Na} + \underset{\text{Deutron}}{{}^{2}_{1}H} \xrightarrow[-{}^{1}_{1}H]{} \underset{\text{Radioactive isotope}}{{}^{24}_{11}Na} \xrightarrow{\text{Disintegrates}} \underset{\text{Stable}}{{}^{24}_{12}Mg} + \underset{\beta\text{-particle}}{{}^{0}_{-1}e}$$

13.9. SYNTHETIC ELEMENTS

Artificial transmutation techniques have been used to synthesise new elements like *technetium, astatine* and *transuranic elements, i.e.* elements with atomic number greater than 92 and follow uranium in the periodic table. Such elements either do not exist in nature as such or exist only in traces. Such elements are called **synthetic elements.** The nuclear reactions for the production of some of the synthetic elements are given below :

$$\underset{\text{Uranium}}{{}^{238}_{92}U} + {}^{12}_{6}C \longrightarrow \underset{\text{Californium}}{{}^{246}_{98}Cf} + 4\,{}^{1}_{0}n$$

$$\underset{\text{Uranium}}{{}^{238}_{92}U} + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U \longrightarrow \underset{\text{Neptunium}}{{}^{239}_{93}Np} + {}^{0}_{-1}e$$

$$\underset{\text{Molybdenum}}{{}^{96}_{42}Mo} + {}^{2}_{1}H \longrightarrow \underset{\text{Technetium}}{{}^{97}_{43}Tc} + {}^{1}_{0}n$$

$$\underset{\text{Plutonium}}{{}^{239}_{94}Pu} + {}^{4}_{2}He \longrightarrow \underset{\text{Curium}}{{}^{242}_{96}Cm} + {}^{1}_{0}n.$$

13.10. NUCLEAR FISSION

In the previous section, it has been pointed out that when a nucleus is bombarded with some sub-atomic particles such as *α-particles, neutrons, protons,* etc., these particles are either captured by the target nucleus or the nucleus disintegrates ejecting some other sub-atomic particles. The new element formed has mass either *slightly greater than or slightly smaller* than that of the parent element. In 1939, it was observed by Hahn and Strassmann that when uranium-235 is hit by slow neutrons, it splits into a number of fragments each of which has mass much smaller than that of uranium. The two main fragments formed are *barium* and *krypton.* Usually 2 or 3 neutrons are also ejected from every target uranium atom. The process is accompanied by the liberation of a large amount of energy. The reaction may be written as

$${}^{235}_{92}U + {}^{1}_{0}n \longrightarrow {}^{140}_{56}Ba + {}^{93}_{36}Kr + 3\,{}^{1}_{0}n$$

The process of splitting of a heavier nucleus like that of uranium-235 into a number of fragments of much smaller mass, by suitable bombardment with sub-atomic particles is called nuclear fission.

When uranium-235 is bombarded with slow neutron, uranium-236 is formed which being unstable, further breaks up in several different ways as described below :

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$$^{235}_{92}U + ^{1}_{0}n \longrightarrow [^{236}_{92}U] \longrightarrow \begin{cases} ^{140}_{56}Ba + ^{93}_{36}Kr + 3^{1}_{0}n \\ ^{144}_{54}Xe + ^{90}_{38}Sr + 2\,^{1}_{0}n \\ ^{144}_{55}Cs + ^{90}_{37}Rb + 2^{1}_{0}n \end{cases}$$

The splitting of ^{235}U has been shown in Fig. 13.3.

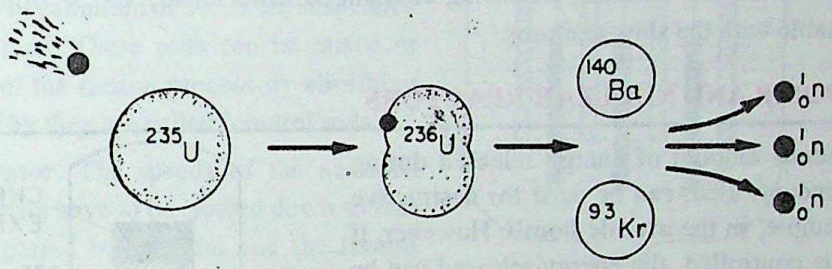

Fig. 13.3. Fission of ^{235}U.

The tremendous amount of energy released during nuclear fission is because of the loss in mass. The sum of the masses of the *fragments produced* and *neutrons released* as a result of fission is less than the sum of the masses of *target* ^{235}U and *bombarding neutron*. The loss in mass gets converted into energy according to Einstein equation,

$$E = mc^2$$

where, m is mass, c is velocity of light, E is energy.

For example, let us calculate the loss of mass when ^{235}U-nuclide splits up into ^{144}Ba and ^{90}Kr along with the release of two neutrons.

$$\underbrace{\begin{matrix} ^{235}_{92}U & + & ^{1}_{0}n \\ 235.118 & & 1.009 \end{matrix}}_{236.127\ \text{amu}} \longrightarrow \underbrace{\begin{matrix} ^{144}_{56}Ba & + & ^{90}_{36}Kr & + & 2^{1}_{0}n \\ 143.881 & & 89.947 & & 2.018 \end{matrix}}_{235.846\ \text{amu}}$$

Thus, mass defect or mass converted into energy is given by

$$\Delta m = 236.127 - 235.846 = 0.281 \text{ amu}$$

But we know, *1 amu = 931.48 MeV*

$\therefore$ $\Delta m = 0.281$ amu $= 931.48 \times 0.281 =$ **261.75 MeV.**

Hence, for every uranium atom undergoing fission, the energy released is approximately 261.75 MeV which corresponds to about 8×10^7 kJ per gram of uranium.

The Nuclear Chain Process

The neutrons emitted from the fission of first uranium atom hit other uranium nuclei and cause their fission resulting in the release of more neutrons which further continue the fission process. In this way, *a nuclear chain reaction* sets up releasing tremendous amount of energy.

If the chain reaction takes place completely as mentioned above, the energy released would be extremely high. However, some of the released neutrons escape from the surface unused and do not involve in the chain process. In spite of this, the net amount of energy released is quite high. It has been found that the energy available from 1 kg of uranium-235 is equivalent to that available from 2×10^4 kg of coal.

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Concept of Critical mass. One of the important aspect of the chain process is that in order to continue or sustain the chain nuclear process there should be sufficient *fissionable material. The minimum amount that the fissionable material must have so as to continue the chain reaction process under the given set of conditions is* called the **critical mass.** If the mass of the material is more than the critical mass, it is referred to as **super-critical mass** whereas if the mass of the fissionable material is smaller than the critical mass, it is called **sub-critical mass.** The critical mass of *U-235* is between *1 kg to 100 kg.*

It may be noted that the naturally occurring uranium contains mostly U-238 isotope (about 99.3%) which is not fissionable with the slow neutrons.

13.11. ATOMIC BOMB AND NUCLEAR REACTORS

The tremendous amount of energy released during fission process if uncontrolled, can be used for destructive purposes as for example, in the **atomic bomb.** However, if the chain reaction is controlled, the energy released can be used for constructive purposes as for example, in the **nuclear reactor.** The principle of each of these devices is briefly explained as follows :

1. Atomic Bomb

Nuclear chain fission reaction is the basic principle of atomic bomb. Two pieces of a *fissionable material* like (*U-235* or *Pu-239*) each with sub-critical mass (< critical mass) are brought together rapidly by means of a conventional explosion.

One piece of the fissionable material constitutes the *wedge* while the other forms a *target.* A chemical explosive is packed at the back of the wedge which can push the wedge to the target. When the wedge and target are brought together, the sub-critical masses constitute **supper-critical mass.** The chain reaction is started by a stray neutron.

The arrangement in its simple form is shown in Fig. 13.4.

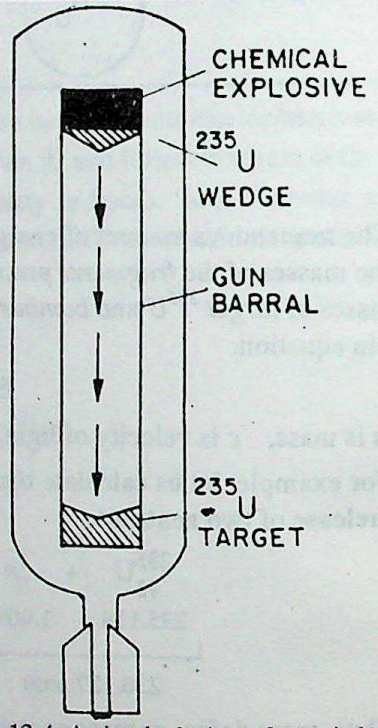

Fig. 13.4. A simple design of atomic bomb.

2. Nuclear Reactors

An equipment in which the nuclear chain reaction is carried out in a controlled manner is called **nuclear reactor.** The energy liberated in a controlled manner is used to produce steam which can run turbines and produce electricity. In nuclear reactors, the nuclear fission is controlled by controlling the number of neutrons released during the fission. Controlling of neutrons is based upon the fact that *cadmium* and *boron* can absorb neutrons to form the corresponding isotopes which are not radioactive.

$$^{113}_{43}Cd + ^{1}_{0}n \longrightarrow ^{114}_{43}Cd + \gamma\text{-ray}$$

$$^{10}_{5}B + ^{1}_{0}n \longrightarrow ^{11}_{5}B + \gamma\text{-ray}$$

The main part of the nuclear reactor called the **reactor core** is shown in Fig. 13.5. It consists essentially of the following parts :

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(*a*) **Fuel rods.** The fissionable material used in the reactor is called *fuel*. The fuel used is *enriched uranium-235* (in the form of U_2O_3). The solid fuel is made into *rods* or *pellets*, which are *shielded* by placing in stainless steel tubes.

(*b*) **Control rods.** To control the fission process, rods made of cadmium or boron are suspended between the fuel rods. These rods can be raised or lowered and control the fission process by absorbing neutrons. That is why they are called 'control rods'.

(*c*) **Moderator.** The speeds of the neutrons produced in the fission have to be slowed down so that they are easily captured by the fuel and the fission process can take place most efficiently. This is done by surrounding the fuel rods with heavy water (D_2O). The material used to slow down the neutrons (without absorbing them) is called a **'moderator'**. Besides heavy water, graphite is also a good moderator.

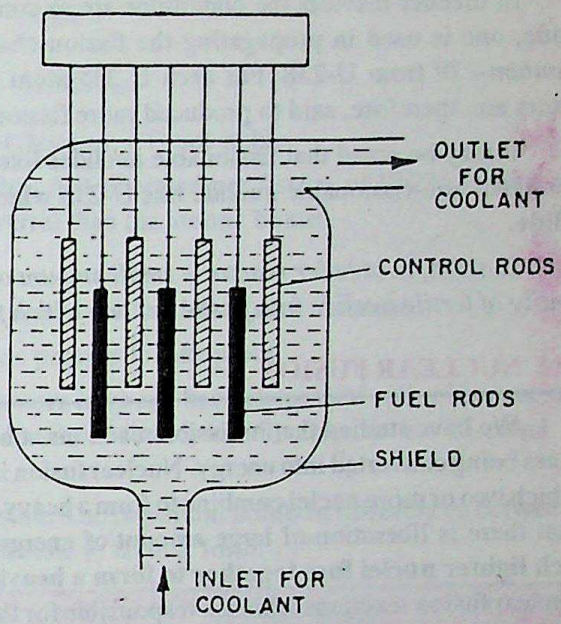

Fig. 13.5. Reactor core.

(*d*) **Coolant.** To carry away the heat produced during fission, a liquid is circulated in the reactor core. This liquid enters the base of the reactor core and leaves at the top. The heat carried by the outgoing liquid is used for producing steam. As a result the liquid cools down and is pumped back to the base of the reactor core. The liquid, thus, used is called **'coolant'**. Usually the coolant used is *heavy water* so that it may also act as a moderator.

(*e*) **Shield.** To prevent the losses of heat and to protect the persons operating the reactor from the radiation and heat, the entire reactor core is enclosed in a heavy steel or concrete dome, called the 'shield'.

In nuclear power plants, the large amount of energy which is released in the form of heat during controlled fission process is converted into electrical energy. In India, four such plants have been set up, one each at *Tarapur, Kotah, Narora* and *Kalpakkam.*

Breeder Reactors

We have become familiar with the fact that U-235 is used as a fuel in nuclear reactors. Naturally occurring uranium consists of only 0.7% of fissionable material, *i.e., uranium-235.* The rest being *uranium-238* which is not fissionable. Thus, natural uranium has to be enriched with fissionable material to be used as a nuclear fuel. Scientists have found *plutonium- 239* and *uranium-233* as other fissionable materials which can be used as fuel in nuclear reactors. These fissionable materials can be produced by the bombardment of more abundantly available U-238 or Th-232 (*which are non-fissionable*) with neutrons. The reactors in which this conversion is carried out are referred to as **breeder reactors.** For example, the production of *Pu-239* from *U-238* by bombarding it with neutron is shown below by the following sequence of reactions

$$\underset{\text{Non-fissionable}}{{}^{238}_{92}U} + {}^{1}_{0}n \longrightarrow {}^{239}_{92}U \longrightarrow {}^{239}_{92}Np + {}^{0}_{-1}e$$

$$\underset{\text{Fissionable}}{{}^{239}_{93}NP \longrightarrow {}^{239}_{94}Pu} + {}^{0}_{-1}e$$

$$\underset{\text{Fissionable}}{{}^{239}_{94}Pu} + {}^{1}_{0}n \longrightarrow \text{fission products + neutrons}$$

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In breeder reactors the conditions are so controlled that out of the 3 neutrons emitted by each U-235 nuclide, one is used in propagating the fission chain with U-235 while the other 2 are used in producing *plutonium-239* from U-238. For each U-235 atom the two Pu-239 atoms are, thus, produced. The breeder reactors are, therefore, said to produced more fissionable nuclei than they consume.

It may be noted that fissionable nuclides like *U-235* or *Pu-239* are also called **fissile nuclides.** On the other hand, non-fissionable nuclide like *U-238* which can be converted into **fissile nuclide** is called a **fertile nuclide.**

In short, in *breeder reactor a small amount of fissile nuclide provides the neurons that convert a large quantity of fertile nuclide into fissile nuclide which further participates in self-sustaining chain reaction.*

13.12. NUCLEAR FUSION

We have studied that in fission reactions, a heavy nucleus splits into smaller fragments and difference in mass being converted into energy. Nuclear fusion is opposite to nuclear fission in the sense that it is a reaction in which two or more nuclei combine to form a heavy nuclide. However, the similar aspect of both the processes is that there is liberation of large amount of energy. Thus, **nuclear fusion** may be defined as a **process in which lighter nuclei fuse together to form a heavier nucleus.** Like nuclear fission, mass defect also occurs in nuclear fusion reactions which is responsible for the tremendous amount of energy released. Some examples of nuclear fusion reactions are :

Fusion reaction	*Mass decrease (amu)*	*Energy released (kJ/mol He)*
${}^{2}_{1}H + {}^{2}_{1}H \longrightarrow {}^{4}_{2}He$	0.026	23×10^{8}
${}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n$	0.012	17.2×10^{8}
$4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{+1}e$ (Positron)	0.029	26×10^{8}

Nuclear fusion reactions require very high temperature, *generally* > 10^{6} *K* in order to overcome electrostatic repulsion between the nuclei when they come together to fuse. The nuclear fusion reactions, therefore, are also called **thermonuclear reactions.**

The high temperature required for fusion to start can be made available only by *nuclear fission process.*

Hydrogen Bomb

The nuclear fusion is the basic principle involved in the preparation of hydrogen bomb.

A hydrogen bomb consists of an arrangement of *nuclear fission* in the centre. It is surrounded by a mixture of deuterium (${}^{2}_{1}H$) and lithium-6 isotope (${}^{6}_{3}Li$). The nuclear fission provides heat and neutrons. The neutrons are used in converting lithium isotope into tritium (${}^{3}_{1}H$) and the heat liberated is used for the fusion between ${}^{2}_{1}H$ and ${}^{3}_{1}H$ to start. The fusion reactions are then accompanied by the liberation of a large amount of energy. The reactions taking place in a hydrogen bomb may be represented as follows :

Fission (*in the centre*) $\longrightarrow$ **Heat + neutrons**

$${}^{6}_{3}Li + {}^{1}_{0}n \longrightarrow \underset{\text{Tritium}}{{}^{3}_{1}H} + {}^{4}_{2}He + 4.78\ MeV$$

$$\underset{\text{Deuterium}}{{}^{2}_{1}H} + \underset{\text{Tritium}}{{}^{3}_{1}H} \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n + 17.6\ MeV$$

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$$^{2}_{1}H + ^{2}_{1}H \longrightarrow ^{3}_{2}He + ^{1}_{0}n + 3.3 \text{ MeV}$$

$$^{3}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + 2^{1}_{0}n + 11 \text{ MeV}$$

Tritium has to be prepared within the hydrogen bomb because it is not stable.

Though the energy liberated per fusion is smaller than that liberated per fission of U-235 (which is about 200 MeV), yet the hydrogen bomb is much more powerful than the atomic bomb.

It is due to following reasons :

(*i*) Mass per atom of deuterium as well as tritium is much smaller than that of uranium.

(*ii*) There are no restrictions of critical mass for fusion process to take place.

It may be noted that the attempts to make **fusion reactors** have not been successful so far because of the many technical difficulties involved. However, if a solution if found, it will place at our disposal a treniendous source of energy at a very cheap rate.

Difference between nuclear fission and nuclear fusion. The important points of differences between nuclear fission and nuclear fusion have been summed up as below in tabular form.

Nuclear fission	*Nuclear fusion*
1. It involves the splitting of a heavy nucleus into lighter nuclei.	It involves the union of two or more lighter nuclei to form a heavy nucleus.
2. It is a chain process.	It is not a chain process.
3. High temperature is not essential.	Being a thermonuclear process, it requires extremely high temperature (> 10^6 K).
4. Fission process can be carried out in a controlled manner and energy released can be used for peaceful purposes.	Fusion process is extremely difficult to be carried in a controlled manner.
5. There is a production of large number of radioisotopes and large amount of nuclear waste is left.	No nuclear waste is left.

13.13. APPLICATIONS OF RADIOACTIVITY AND RADIOISOTOPES

It has already been pointed out that each radioactive isotope has a specific half-life period. The radiations that it emits can be detected and measured. Also the chemical properties of isotopes of a given element are identical. This makes it possible to incorporate a small amount of radioisotopes in a *system* and *trace* the fate of particular element or a compound in a series of chemical or physical changes. Radioisotopes have large number of applications in different fields like medicine, engineering, biology, chemistry, archeology, agriculture and industry. Some of the applications of radioactivity have been discussed as follows :

1. **Age of minerals and rocks.** In section 13.6, we have discussed that the end product in natural radioactive disintegration series is an *isotope of lead.* Each disintegration step has a definite *half-life* and hence a definite *decay constant.* Thus, by determining the amounts of parent radioactive element and the isotope of lead in a sample of rock, the age of rock can be calculated. For example, if we wish to determine the age of rock containing $^{238}_{90}U$ (*half life* = 4.5×10^9 *years*), we measure the ratio of the concentrations of $^{238}_{90}U$ and its end product $^{206}_{82}Pb$. We assume that the rock did not contain any *lead isotope* initially.

Suppose, the ratio of uranium-238 and lead-206 is *unity*. It implies that half of the uranium originally present has been converted into lead isotope. The age of rock must therefore be equal to the half-life of

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uranium-238 *i.e.* 4.5×10^9 years. Pb/U ratio of most of the rocks is 1.33×10^{-2} indicating that their age is of the order of 10^8 years.

Age of earth. The abundance ratio of the two isotopes of uranium, *i.e.*, $^{235}U : ^{238}U$ at present is 1 : 140. The half-life period of ^{235}U is 7×10^8 years. Assuming that in the beginning the proportion of two isotopes was equal, the above data determines the age of earth as 5×10^9 years.

Example 13.4. *A sample of pitch blende contains 0.05 g of ^{206}Pb for every gram of ^{238}U present in it. Calculate the age of the rock ($t_{1/2}$ of $^{238}U = 4.6 \times 10^9$ years).*

Solution. $t_{1/2} = 4.5 \times 10^9$ years

$$\lambda = \frac{0.693}{4.5 \times 10^9} \text{ year}^{-1}$$

Amount of ^{238}U present at the time of analysis (N_t) = 1 g

Amount of ^{238}U originally present (N_0)

$$= \begin{bmatrix} \text{Amount of } ^{238}\text{U now} \\ \text{present} \end{bmatrix} + \begin{bmatrix} \text{Amount of } ^{238}\text{U changed} \\ \text{into } ^{206}\text{Pb} \end{bmatrix}$$

$$= 1 \text{ g} + \frac{238}{206} \times 0.05 \text{ g}$$

$$= 1 \text{ g} + 0.0577 \text{ g} = 1.0577 \text{ g.}$$

Let t be the time in which 1.0577 g of ^{238}U is reduced to 1 g of ^{238}U.

Now apply the relationship, $t = \frac{2.303}{\lambda} \log \frac{N_0}{N_t}$

$$= \frac{2.303}{0.693} \times 4.5 \times 10^9 \times \log \frac{1.0577}{1}$$

$$= \mathbf{3.64 \times 10^8 \text{ years.}}$$

REVIEW PROBLEMS

13.15. A mineral rock contains 0.257 mg of Pb-206 for each milligram of ^{238}U. Calculate the age of the rock if half life period of ^{238}U is 4.5×10^9 years.

13.16. A sample of uranium ore is found to contain 5 mg of U-238 and 1.80 mg of Pb-206. Calculate the age of the uranium rock. $t_{1/2}$ of U-238 is 4.5×10^9 years.

13.17. A rock is found to contain U-238 and Pb-206 in the ratio of 3 : 2, if $t_{1/2}$ of U-238 is 4.5×10^9 years, find the age of the rock.

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2. Radio Carbon Dating. It is a method of determining the ages of the *archeological objects* (wood, dead plants and animals). This technique was developed by Willard Libby. It helps in determining the date at which a particular plant or animal died. Libby was awarded Nobel Prize for his technique.

The *principle* of this technique lies in the fact that due to bombardment of cosmic rays, nitrogen atoms present in the upper atmosphere are converted into radioactive carbon, ^{14}C according to the reaction :

$$^{14}_{7}N + ^{1}_{0}n \longrightarrow ^{14}_{6}C + ^{1}_{1}H$$

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Carbon-14 is radioactive and has half-life period of 5770 years. It is oxidised in the air to give radioactive carbon dioxide. Thus, the atmospheric carbon dioxide contains a small proportion of ^{14}C carbon dioxide ($^{14}CO_2$) which is assimilated by plants and animals. Living plants and animals have a definite and constant proportion of ^{12}C and ^{14}C. When plant or animal dies, no fresh $^{14}_{6}C$ nuclei as $^{14}CO_2$ are received by the plant or animal. The ^{14}C present in these, decays according to the reaction

$$^{14}_{6}C \longrightarrow {}^{14}_{7}N + {}^{0}_{-1}e; \quad t_{1/2} = 5770 \text{ years.}$$

The amount of ^{14}C in a sample can be accurately determined by counting the number of β-particles emitted per minute by one gram of the sample. By knowing ^{14}C content and half-life period, the age of the sample can be determined.

It may be noted that *older the sample is,* smaller is $^{14}_{6}C$ *count rate.* Ages of samples upto 50,000 years old can be determined accurately by this method.

Example 13.5. *A sample of wood from archeological find has 5.00 counts per minute per gram of carbon. Calculate the age of the wood sample. A freshly cut wood gives 15.3 counts per minute per gram of carbon. Half life of ^{14}C is 5770 years.*

Solution.

$$t_{1/2} = \frac{0.693}{\lambda}$$

$$\therefore \quad \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770} = 1.201 \times 10^{-4} \text{ year}^{-1}$$

Since the rate of count is directly proportional to the number of atoms.

Therefore,

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N_t} = \frac{2.303}{1.201 \times 10^{-4}} \log \frac{15.3}{5} = \mathbf{9313 \text{ years.}}$$

Example 13.6. *An old chair of wood shows $^{14}_{6}C$ activity which is 80% of the activity found today. Find the age of the old chair of wood. Half life period of ^{14}C is 5770 years.* (A.I. CBSE 1991)

Solution. Suppose the amount of ^{14}C present in the wood originally (*i.e.*, same as the wood has today)

$$= x$$

The amount of ^{14}C present in old chair of wood

$$= \frac{80}{100} x = 0.8x$$

Let t be time in which ^{14}C changes from x to $0.8x$

Now,

$$t_{1/2} = \frac{0.693}{\lambda}$$

$$\therefore \quad \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{5770}$$

$$= 1.201 \times 10^{-4} \text{ year}^{-1}$$

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N_t} = \frac{2.303}{1.201 \times 10^{-4}} \log \frac{x}{0.8x}$$

$$= \frac{2.303}{1.201} \times 10^4 \times 0.0969 = 1.858 \times 10^3 \text{ years.}$$

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Example 13.7. *2.0 microgram of phosphorus-32 was injected into a living system for biological tracer studies. The half-life period of $^{32}_{15}P$ is 14 days. How long will it take the radioactivity to fall to 10% of initial value ?* [CBSE (1) 1992]

Solution.

$$t_{1/2} = \frac{0.693}{\lambda}$$

$$\therefore \quad \lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{14 \text{ days}} = 0.0459 \text{ days}^{-1}$$

Let t be the time in which radioactivity falls to 10% of original value

Now,

$$t = \frac{2.303}{\lambda} \log \frac{N_0}{N} = \frac{2.303}{\lambda} \log \frac{100}{10}$$

$$= \frac{2.303}{0.0495} \times \log (10) = \frac{2.303}{0.0495}$$

$$= \mathbf{46.5 \text{ days.}}$$

REVIEW PROBLEMS

13.18. A piece of wood shows a C-14 activity, which is 70% of the activity found in fresh wood of today. Calculate the age of the piece of wood. ($t_{1/2}$ for $^{14}_{6}C$ is 5770 years). ***(CBSE 1993)***

13.19. The $^{14}_{6}C$ to $^{12}_{6}C$ ratio in a wooden article is 13% that of the atmosphere. Calculate the age of the wooden article. Given that half-life of ^{14}C as 5770 years.

13.20. A sample of carbon from a wood recovered in excavation is found to give seven counts per minute per gram of carbon. What is the approximate age of wood ? The original count rate is 15.3 and $t_{1/2}$ is 5770 years.

13.21. A piece of preserved hair has 40% as much ^{14}C as a fresh one has today. Calculate the approximate life of the hair $t_{1/2}$ of C-14 is 5770 years.

13.22. A living plant acquires a definite fraction of C-14 nuclei. If the freshly cut wood gives 16.3 counts per min. per gram and an old wooden bowl gives 9.3 counts what is the age of wooden bowl ? $t_{1/2}$ of C-14 is 5770 years.

13.23. A sample of wood has an activity of 2.5 disintegrations per second. A freshly cut wooden tree have an activity of 10 disintegration per second. Estimate the age of the wood sample. The half life of C-14 is 5730 years. ***[CBSE (2) 1992]***

13.24. What is the age of a vegetarian beverage whose tritium content is only 15% of the level in living plants ? The half life of tritium is 12.3 years. ***(PSEB 1993)***

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3. Tracer Techniques. Radio isotopes are frequently used *as tracers* or *tagged atoms* in may processes in different fields like surgery, medicine, agriculture, industry and chemistry. In tracer technique, a radioactive isotope is added to the reactants and its movement is studied by measuring radioactivity in different parts. The common examples of tracer techniques are :

(*i*) **In medical diagnosis.** For example, in order to find out if blood is circulating to a wound or not, a radioactive isotope is injected into the blood stream. After suitable time gap, the blood from the wound is examined for its radioactivity. If no radioactive isotope is detected, it means that passage of blood is hindered. The rate of circulation of blood can also be detected by this method.

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Tracer technique is also used for the detection of *thyroid disorder* and *brain tumours.*

(*ii*) **In Agriculture,** the uptake of phosphorus by plants is studied by mixing radioactive phosphorus with phosphatic fertilizers.

(*iii*) **In Chemistry,** tracer techniques can be used :

(*a*) to find the solubility of sparingly soluble salt. For example, solubility of lead sulphate can be determined by using a known amount of radioactive lead ;

(*b*) to study the mechanism of a particular reaction or to develop the structure of a particular chemical species.

4. Cancer Therapy. γ-rays emitted by the radio isotopes can be used in the treatment of cancer. The basis of such a treatment is, that the radiation tend to destroy cancerous cells more easily than the normal cells. Thus, a carefully controlled beam of γ-rays of appropriate doses may be used to arrest the growth of cancerous cells.

5. Neutron activation analysis. This method is gaining importance in *analytical chemistry these days* because it can help in the detection of even one part of the element per billion parts of the sample. In this method, a non-radioactive sample is bombarded with neutrons and element of interest (*i.e.*, element whose amount in the sample is to be determined) is converted (activated) into its radioactive isotope. The radioactivity of this radioisotope is measured. Quantitative measurement of radioactivity and the knowledge of other factors such as *half-life of radioisotope, efficiency of radiation detector,* rate of *neutron bombardment,* etc., help in the calculation of the amount of the element in the sample. This method is quite advantageous because :

(*i*) trace amounts of the elements can be determined ;

(*ii*) a sample can be tested without destroying it ; and

(*iii*) the sample can be in any state of matter including biological material.

13.14. HAZARDS OF RADIATIONS

Although the nuclear radiations are quite useful to mankind, yet they are one of the major causes of atmospheric pollution. When living organisms are exposed to these radiations, the complex organic molecules in the body get ionised, break up and ultimately disrupt the normal functioning of the living organism. The damage caused by the radiations, however, depends upon the doses of radiations received. The radiations damage the living organisms in the following ways :

(*a*) **Pathological damage.** It is a permanent damage produced in the body which ultimately leads to death. Larger doses of radiations cause immediate death whereas smaller doses can cause the development of diseases like cancers or leukemia which are fatal.

(*b*) **Genetic damage.** This type of damage is produced when radiations affect the chromosomes of the cellular nuclei and injure the genes in reproductive cells.

On of the major problem before the scientists is to check and deal with the radioactive waste formed in nuclear reactors. Any accidental leakage of the radioactive radiations can prove to be disastrous. One such accident occurred in 1986 in U.S.S.R. which led to many deaths and caused injuries to several others.

SOME MISCELLANEOUS PROBLEMS

Example 13.8. *Calculate the energy released in the nuclear fusion reaction* ${}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n$.

The atomic masses are ${}^{2}_{1}H = 2.014$; ${}^{3}_{1}H = 3.016$; ${}^{4}_{2}He = 4.003$; ${}^{1}_{0}n = 1.009$ *(all in amu).* [A.I. CBSE (O) 1990]

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Solution. The given fusion reaction is

$$^{2}_{1}H + ^{3}_{1}H \longrightarrow ^{4}_{2}He + ^{1}_{0}n$$

Mass of the reactants $= 2.014 + 3.016 = 5.030$ amu

Mass of the products $= 4.003 + 1.009 = 5.012$ amu

Loss of mass $= 5.030 - 5.012 = 0.018$ amu

The energy produced $= 0.018 \times 931.48$ MeV ($\because$ 1 amu = 931.48 MeV)

$= \mathbf{16.76}$ **MeV per He atom.**

The energy in kJ mol^{-1} can be calculated as follows :

The energy of fusion $= 16.76 \times 1.602 \times 10^{-16}$ kJ per atom ($1\ MeV = 1.6 \times 10^{-16}\ kJ$)

$= 16.76 \times 1.602 \times 10^{-16} \times 6.02 \times 10^{23}$ kJ mol^{-1}

$= \mathbf{1.616 \times 10^{9}}$ **kJ** $\mathbf{mol^{-1}}$.

Example 13.9. *$^{210}_{84}Po$ decays with α-emission to $^{206}_{82}Pb$ and has a half-life of 138.4 days. If 1.0 g of Po-210 is placed in a sealed tube, how much helium will accumulate in 69.2 days ? Express answer in cm^3 at STP.* (Roorkee Ent. 1991)

Solution. Disintegration constant λ is given by

$$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{138.4 \text{ days}} = 5 \times 10^{-3} \text{ days}^{-1}$$

Now initial mass of Po-210 $= 1.0$ g

Let x g of Po decay in 69.2 days

$\therefore$ Amount of Po left after 69.2 days $= (1 - x)$ g.

Now $$\lambda = \frac{2.303}{t} \log \frac{a}{a - x}$$

or $$\log \frac{1}{1 - x} = \frac{\lambda t}{2.303} = \frac{5 \times 10^{-3} \times 69.2}{2.303} = 0.150$$

$$\frac{1}{1 - x} = \text{antilog } (0.150) = 1.413$$

or $$1 - x = \frac{1}{1.413} = 0.708$$

or $$x = 1 - 0.708 = 0.292 \text{ g}$$

$\therefore$ amount of Po-210 disappeared $= 0.292$ g

$$^{210}_{84}Po \longrightarrow ^{206}_{82}Pb + ^{4}_{2}He$$

210 g of Po produce He $= 22400$ cm^3 at STP

0.292 g of Po produce He $= \frac{22400}{210} \times 0.292$

$= \mathbf{31.14}$ $\mathbf{cm^3}$ **at STP.**

Example 13.10. *A sample of Mo-90 is observed to have an activity of 346 disintegrations min^{-1}. What is the activity in μC$_i$. If $t_{1/2}$ of Mo-99 is 66.6 hr, how many grams of Mo-99 is present in the sample ?*

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Solution. **Curie** (C_i) is the unit of measuring radioactivity

$$1 \text{ curie} = 1\ C_i = 3.7 \times 10^{10} \text{ disintegration per second } (ds^{-1})$$

$$1 \text{ microcurie} = 1\ \mu C_i = 3.7 \times 10^4\ ds^{-1}$$

Activity of radioactive element refers to the rate of radioactive decay.

Step I. *Determination of activity in* μC_i

Now activity of the sample $= \left(\dfrac{346 \text{ min}^{-1}}{60 \text{ s min}^{-1}}\right) \times \dfrac{1\ \mu C_i}{3.7 \times 10^4 \text{ s}^{-1}}$

$$= \mathbf{1.558 \times 10^{-4}}\ \mu C_i.$$

Step II. *Determination of* λ

$$t_{1/2} = \frac{0.693}{\lambda}$$

or $$\lambda = \frac{0.693}{t_{1/2}} = \frac{0.693}{66.6 \times 60} \text{ min}^{-1} = 1.73 \times 10^{-4} \text{ min}^{-1}.$$

Step III. *Calculation of mass of Mo-99*

Now Activity $A = \lambda N$

$\therefore$ $$N = \frac{A}{\lambda} = \frac{346 \text{ min}^{-1}}{1.73 \times 10^{-4} \text{ min}^{-1}}$$

$$= 200 \times 10^4 \text{ atoms} = 2 \times 10^6 \text{ atoms}$$

6.02×10^{23} Mo atoms posses mass $= 99$ g

2×10^6 atoms weigh $= \dfrac{99}{6.02 \times 10^{23}} (2 \times 10^6 \text{ g})$

$$= 32.9 \times 10^{-17} \text{ g} = \mathbf{3.29 \times 10^{-16}\ g.}$$

SOME IMPORTANT TERMS CONCEPT AND FORMULAE

- **Radioactivity.** Spontaneous emission of active rays by certain unstable elements.
- **Alpha-particles.** He^{2+} ion (Helium nuclei).
- **Beta-rays.** Consist of electrons.
- **Gamma-rays.** High energy electromagnetic rays.
- **N/P Ratio.** Stable nuclei have N/P ratio in the range 1 – 1.6.
- **Group Displacement Law.** When a nucleus emits an alpha particle, the daughter element formed lies two places left to the parent element and when it emits a beta particle, the daughter element lies one place right to the parent element.
- Emission of a β-particle results in the formation of an **isobar** of the parent element.
- Emission of α-particle results in the formation of **isodiapher** of the parent nuclide.
- Emission of one α-particle and two β-particles in succession leads to the formation of an **isotope** of the parent element.
- **Decay constant,** $\lambda = \dfrac{2.303}{t} \log \dfrac{N_0}{N_t}$

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- **Isosters.** The species with same number of atoms and same number of electrons *e.g.*, CO_2, N_2O.
- **Isodiaphers.** The species with same value of isotopic number (A – 2Z).
- **Nuclear isomers.** The nuclides with same values of A and Z but having different quantum states or energy states.
- **Half life period,** $t_{1/2} = \frac{0.693}{\lambda}$

  Half-life period does not depend upon the amount of the radioactive substance.
- **Activity.** The rate nuclear disintegration.

$$\text{Activity} = -\frac{dN}{dt} = \lambda N.$$

- **Units of Activity.**

1 Bacqueral (Bq) = 1 disintegration per second

Curie (C_i) = 3.7×10^{10} dis/sec = 3.7×10^{10} Bq

- The first **artificial transmutation** was carried out be Rutherford.

$$^{14}_{7}N + ^{4}_{2}He \longrightarrow ^{17}_{8}O + ^{1}_{1}H.$$

EXERCISE

VERY SHORT-ANSWER QUESTIONS
(1 Mark)

1. What is the final product formed in disintegration of $^{238}_{92}U$?
2. Which radioactive radiation is not deflected by electrical or magnetic field ?
3. What change of mass is produced by emission of α-particle ?
4. What is meant by $4n + 2$ series ?
5. Which order is followed by radioactive decay ?
6. The half-life period of two radioactive element A and B are respectively 42 and 32 days. Which is more stable ?
7. Which bombarding projectile has been used in following transformation ?

$$^{209}_{83}Bi + ... \longrightarrow ^{210}_{84}Po + ^{1}_{0}n.$$

8. What is the relationship between average life period and half-life period of radioactive element ?
9. What is the critical mass of $^{235}_{92}U$?
10. Starting with one g of radioactive sample, 0.25 is left after 10 days. Calculate the time required for one half of sample to decay. *[CBSE (3) 1992]*
11. $^{232}_{90}Th$ emits one α-particle and two β-particles what will be the daughter element ? *[Har. (Sc.) 1992]*
12. What is the unit of radioactivity ? *(H.P. Board 1992)*
13. What are particle accelerators ? *(A.I. CBSE 1993)*
14. Complete the nuclear reaction, $^{14}_{7}N$ (α, ...) $^{17}_{8}O$. *(A.I. CBSE 1995)*
15. Give the equation for the first artificial transmutation.

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16. What is moderator ?
17. What is the fuel used in nuclear reactors ?
18. What is the relation between half-life time and mean life time ?

DESCRIPTIVE QUESTIONS
(2—3 Marks)

19. Name three chief kinds of radiations that are emitted from radioactive element. Compare their properties.
20. What changes are caused in atomic number and mass number of the parent atom when α and β-particles are emitted ? Give examples.
21. A nucleus does not have any electron yet a β-particle is emitted from the nucleus. How do you justify it ?
22. State and explain the group displacement law. **[*Pb. S.B. 1992 ; Har. (Sc.) 1992*]**
23. Write the nuclear equations for the following transformations :
    (*i*) Lead-212 emits a β-particle.
    (*ii*) Uranium-238 emits an α-particle followed by emission of two β-particles.
    (*iii*) Thorium-232 decays to radium-228.
24. What is meant by the term Radioactive disintegration series ? How many α and β-particles are emitted in all when uranium 238 decays to lead-206 ?
25. Define the term half-life period. Is it dependent on the initial amount of radioactive substance ? What is the relationship between half-life period and decay constant ?
26. What is meant by artificial transmutation ? What kind of particles are used for carrying out such a process ? Give suitable example.
27. Why positively charged projectiles are given high energies before bombarding the atomic nuclei ?
28. What is the difference between natural radioactivity and induced radioactivity ?
29. Explain the principle of breeder reactor. **[*A.I. CBSE (O) 1991*]**
30. Complete the following :
    (*i*) $^{246}_{96}Cm + ^{12}_{6}C \longrightarrow ..... + 4\,(^{1}_{0}n)$
    (*ii*) $..... (\alpha, 2n) \longrightarrow ^{211}_{85}At$
    (*iii*) $^{96}_{42}Mo\,(..... n) \longrightarrow ^{97}_{43}Tc$
    (*iv*) $^{14}_{7}N\,(\alpha\ .....) \longrightarrow ^{17}_{8}O.$
31. What is the difference between nuclear fission and nuclear fusion ? (Give four points of difference). **(*H.P. Board 1993*)**
32. (*a*) Explain the principle of neutron activation analysis.
    (*b*) Why is neutron activation analysis so useful in contrast to the ordinary methods of analysis ?
33. Give importance of radioisotopes in the field of surgery, chemistry and radio carbon dating.
34. Write short notes on :
    (*i*) Radio carbon dating
    (*ii*) Use of radio isotope in archeology
    (*iii*) Radio isotopes as tracers.
35. Complete the following nuclear equations :
    (*i*) $^{23}_{11}Na + ^{2}_{1}H \longrightarrow ? + ^{1}_{1}H$
    (*ii*) $^{59}_{27}Co + ? \longrightarrow ^{56}_{25}Mn + ^{4}_{2}He$
    (*iii*) $^{238}_{92}U + ^{2}_{1}H \longrightarrow ? + ^{0}_{-1}e$
    (*iv*) $^{246}_{96}Cm + ^{13}_{6}C \longrightarrow ^{254}_{102}No + ?$
    (*v*) $^{238}_{92}U + ^{14}_{7}N \longrightarrow ^{246}_{(...)}Fs + (\ \ )\,^{1}_{0}n$

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36. Write equation to represent each of the following nuclear processes :

(*i*) The reaction of two deutrons to produce a nucleus of ^{3}He.

(*ii*) The production of $^{243}_{97}Bk$ by bombardment of $^{241}_{95}Am$ with α-particle.

(*iii*) The bombardment of ^{121}Sb by α-particle to produce $^{124}_{53}I$ followed by its radioactive decay by positron (β^+) emission.

37. What is meant by artificial transmutation ? ***(Pb.S.B. 1992)***

38. Which of the following nuclear reactions are accompanied by emission of neutrons :

(*a*) $^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P$ (*b*) $^{12}_{6}C + ^{1}_{1}H \longrightarrow ^{13}_{7}N$

(*c*) $^{30}_{15}P \longrightarrow ^{30}_{14}Si + ^{0}_{1}e$ (*d*) $^{241}_{96}Am + ^{4}_{2}He \longrightarrow ^{244}_{97}Bk + ^{0}_{1}e$. ***(I.I.T.J.E.E. 1989)***

39. Describe the principle of atomic bomb and nuclear reactor. ***[A.I. CBSE (O) 1992]***

40. Write complete equations for the following nuclear reactions, $^{14}_{7}N$ (*n*, *p*) and $^{15}_{7}N$ (*p*, α).

41. What is the main use of the following nuclear disintegration ?

$$^{14}_{6}C \longrightarrow ^{14}_{7}N + ^{0}_{-1}e.$$ ***[A.I. CBSE (O) 1990]***

42. Differentiate between nuclear reactions and chemical reactions.

43. Complete the following nuclear reactions :

(*i*) ..... (∝, 2*n*) $^{211}_{85}At$ (*ii*) $^{96}_{42}Mo$ (....., *n*) $^{97}_{43}Tc$

(*iii*) $^{55}_{25}Mn$ (*n*, γ) ..... ***[A.I. CBSE (2) 1994]***

44. Complete the following nuclear reactions :

(*i*) $^{96}_{42}Mo + ^{2}_{1}H \longrightarrow$ ..... + $^{1}_{0}n$ (*ii*) ..... + $^{12}_{6}C \longrightarrow ^{248}_{98}Cf + 4^{1}_{0}n$

(*iii*) $^{27}_{13}Al$ + ... $\longrightarrow ^{30}_{15}P + ^{1}_{0}n$.

45. Why do radioactive elements decay ? ***(Pb. Board 1997)***

46. Half life period of a radioactive element is 100 sec. The value of its disintegration constants is ..... ***(Pb. Board 1997)***

SOME NUMERICAL PROBLEMS

47. A certain radioisotope $^{A}_{Z}X$ ($t_{1/2}$ = 10 days) decays to give $^{A-4}_{Z-2}Y$ and $^{4}_{2}He$. If 1.0 gm-atom of $^{A}_{Z}X$ is kept in a sealed vessel. How much helium will accumulate in 20 days ? Express the result in cm^3 at S.T.P. ***(Roorkee Ent. 1987)***

48. The fission fragments in the neutron fission of U-235 are found to be $^{98}_{42}Mo$ and $^{136}_{54}Xe$. Estimate the particles released during the reaction and also the energy liberated. Given that masses of U-235, Xe-136, Mo-98 and $^{1}_{0}n$ are 235.044, 135.907, 97.90 and 1.0068 amu respectively.

49. The actual atomic mass of $^{40}_{20}Ca$ is 39.96259 amu. Find the binding energy of this nuclide. Mass of neutron is 1.008665 and mass of atomic hydrogen is 1.007825 amu.

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50. 100 mg of Co-60 is stocked in a nuclear laboratory as a γ-ray source. If its half-life is 5.26 years, calculate the percentage decrease in its activity after one year.

51. What is the energy change in J mol^{-1} for the following process :

$$4\,{}^{1}_{1}H \longrightarrow {}^{4}_{2}He + 2\,{}^{0}_{1}e$$

Mass of ${}^{1}_{1}H$ = 1.00728 amu, Mass of ${}^{4}_{2}He$ = 4.00150 amu.

52. 10 gm-atoms of an α-active radioisotope are disintegrating in a sealed container. In one hour, the helium gas collected at STP is 11.2 cm^3. Calculate the half-life of the radioisotope. *(Roorkee Ent. 1989)*

53. Calculate the energy released in the fusion reaction per atom of helium produced

$${}^{2}_{1}H + {}^{3}_{1}H \longrightarrow {}^{4}_{2}He + {}^{1}_{0}n$$

Given the following atomic masses :

${}^{2}_{1}H$ = 2.014 ; ${}^{3}_{1}H$ = 3.016, ${}^{4}_{2}He$ = 4.003 ; n = 1.009 amu and 1 amu = 1.51×10^{-10} J. *[A.I. CBSE (1) 1994]*

54. The half-life of cobalt-60 is 5.26 years. Calculate its percentage activity remaining after 7 years. *[A.I. CBSE (1) 1995]*

55. A wood piece obtained from an archeological source shows a ${}^{14}C$ activity, which is 10% of the activity found in green wood. Calculate the age of the wood piece. $t_{1/2}$ of C-14 = 5770 years.

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FOR THE COMPETITIVE EXAMS

MULTIPLE CHOICE QUESTIONS

Select the correct answer from each of the following questions :

1. Radioactive decay follows

(*a*) first order kinetics (*b*) zero order kinetic

(*c*) second order kinetics (4) third order kinetics.

2. The bombarding projectile in the following transformation is $^{14}_{7}N + ? \longrightarrow ^{14}_{6}C + ^{1}_{1}H$

(*a*) proton (*b*) deutron (*c*) neutron (*d*) $^{0}_{-1}e$.

3. The end product the natural radioactive series designated as $4n$ series is

(*a*) Bismuth (*b*) Thorium (*c*) An isotope of lead (*d*) An isotope of calcium.

4. Which is the missing particle in the following nuclear reaction, $^{7}_{3}Li + ^{2}_{1}H \longrightarrow ^{8}_{3}Li + ?$

(*a*) proton (*b*) deutron (*c*) positron (*d*) α-particle.

5. The following nuclear transmutation :

$$^{23}_{11}Na + ^{1}_{1}H \longrightarrow ^{23}_{12}Mg + ^{1}_{0}n$$

belongs to

(*a*) (n, α) type (*b*) (p, n) type (*c*) (α, n) type (*d*) (d, p) type.

6. If λ is decay constant, then half-life period ($t_{1/2}$) for the radioactive decay is equal to

(*a*) $\lambda/0.693$ (*b*) $0.693/\lambda$ (*c*) $2.303 \log \lambda$ (*d*) $0.693\ \lambda$.

7. Which of the following represents the pair of *isotones* ?

(*a*) protium-deutron (*b*) proton-deutron (*c*) $^{30}_{14}Si, ^{31}_{15}P$ (*d*) $^{32}_{16}S, ^{28}_{14}Si$.

8. To which part of the atom is radioactivity associated ?

(*a*) protons only (*b*) neutrons only (*c*) nucleus (*d*) extranuclear part.

9. The nuclear fission reaction involves the :

(*a*) combination of two nuclei to form a single nuclide (*b*) splitting of single nuclide into two nuclei

(*c*) combination of α and β-particles (*d*) combination of α and deutron.

10. The basic principle used in hydrogen bomb is :

(*a*) Nuclear fission (*b*) Nuclear fusion

(*c*) Nuclear disintegration (*d*) Neutron splitting.

11. The half-life period of a radioactive element depends upon :

(*a*) pressure (*b*) temperature

(*c*) the amount of element present (*d*) none of the above.

12. $t_{1/2}$ of a radioactive element is 5 years. The amount of it remaining out of 10 g in 20 years will be

(*a*) 0.625 g (*b*) 1.25 g (*c*) 0.3125 g (*d*) It will totally disappear.

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13. Which nuclear process has been exploited by the humans for generation of power ?
(*a*) fusion (*b*) transmutation (*c*) fission (*d*) spallation.

14. To which of the following series does Rn-222 belong ?
(*a*) $4n$ series (*b*) $(4n + 1)$ series (*c*) $(4n + 2)$ series (*d*) $(4n + 3)$ series.

15. In the nuclear reaction, $^{238}_{92}U \longrightarrow ^{206}_{82}Pb$, the number of α and β-particles emitted are
(*a*) 7α, 5β (*b*) 6α, 4β (*c*) 4α, 3β (*d*) 8α, 6β.
(CBSE Med. Ent. 1988)

16. The phenomenon of radioactivity was discovered by
(*a*) Madam Curie (*b*) Rutherford (*c*) Pierre Curie (*d*) Henry Becquarel.

17. Which is not emitted by radioactive substance ?
(*a*) α-rays (*b*) β-rays (*c*) positron (*d*) proton. ***(AIIMS 1997)***

18. Positron is
(*a*) electron with positive charge (*b*) a helium nucleus
(*c*) a nucleus with two protons (*d*) a nucleus with one proton and one neutron.
(AIIMS 1997)

19. C-14 dating method is that the
(*a*) C-14 fraction is same is all objects (*b*) C-14 highly insoluble
(*c*) radio carbon-14 and C-12 are constant (*d*) All the above. ***(CBSE Ent. 1997)***

20. $^{215}_{84}Po$ and $^{211}_{82}Pb$ are pair of
(*a*) isotopes (*b*) isotones (*c*) isoesters. (*b*) isodiaphers.

ASSERTION-REASON TYPE QUESTIONS

In each of the following questions two statements are given one labelled as *Assertion A* and the other labelled as *Reason R*. Examine the two statements carefully and mark the correct answer, (*a*), (*b*) (*c*) or (*d*) according to the following instructions :

(*a*) If both A and R are correct and R is explanation of A
(*b*) If both A and R are correct but R is not the explanation of A
(*c*) If A is correct R is wrong
(*d*) If A is wrong R is correct.

21. ***Assertion* A** : α-rays can be stopped by air easily.
***Reason* R** : α-rays are made of helium nuclei.
(*a*) (*b*) (*c*) (*d*)

22. ***Assertion* A** : The reaction $^{8}_{5}B \longrightarrow ^{8}_{4}Be$ takes place due to positron decay.
***Reason* R** : n/p ratio increases in the above change.
(*a*) (*b*) (*c*) (*d*)

23. ***Assertion* A** : The equipment used to carry out the nuclear reaction in a controlled manner is called Breeder reactor.
***Reason* R** : Breeder reactor converts fertile material into fissile material.
(*a*) (*b*) (*c*) (*d*)

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24. ***Assertion* A** : Neutrons are the best bombarding particles.

***Reason* R** : Neutrons are neutral particles.

(*a*) (*b*) (*c*) (*d*)

25. ***Assertion* A** : The basic principle involved in hydrogen bomb is nuclear fission.

***Reason* R** : Attempts to carry out nuclear fusion process in a controlled manner have not been successful.

(*a*) (*b*) (*c*) (*d*)

FILL IN THE BLANKS

1. Out of α, β and γ-rays, the one having maximum penetration power are .....
2. The number of α and β-particles emitted, when the following nuclear transformation occurs

$$^{232}_{92}X \longrightarrow ^{208}_{82}Y$$ are ..... respectively.

3. The particle having a mass of one amu and no charge is represented by the symbol .....
4. The species with different number of nucleons but same number of neutrons are called .....
5. The species with same number of protons but different number of neutrons are called .....
6. $^{27}_{13}Al + ^{4}_{2}He \longrightarrow ^{30}_{15}P + ...$
7. $^{241}_{95}Am + ^{4}_{2}He \longrightarrow ^{244}_{97}Bk + ...$
8. $^{96}_{42}Mo + ^{4}_{2}He \longrightarrow ^{100}_{43}Tc + ...$
9. A radioactive nucleus decays emitting one α and two β-particles. The daughter nucleus is ..... of the parent.

(I.I.T. J.E.E. 1989)

10. The synthetic elements prepared by artificial transmutation have atomic numbers ..... to .....
11. The half life period of radioactive element if 87.5% of it disintegrate in 40 min. is .....

(C.E.E.T. Kurukshetra 1996)

12. The reaction, $^{2}_{1}D + ^{3}_{1}T \longrightarrow ^{4}_{2}He + ^{1}_{0}n$ is an example of .....

TRUE/FALSE STATEMENTS

Pick up true and false statement out of the following :

1. γ-rays are not affected by electrical or magnetic field.
2. The product of artificial transmutation is always a radioactive nuclide.
3. α and β-particles are always emitted simultaneously in radioactive transmutation.
4. β-particles are considered to be best bombarding projectiles.
5. A tremendous amount of energy is produced during nuclear fission as well as in nuclear fusion process.
6. The β-particle emission occurs from the extra nuclear part of the atom.
7. The daughter product formed by the emission of α-particle has mass number less by 4 units than the parent nuclide.
8. In the reaction $^{7}_{3}Li + Z \longrightarrow ^{7}_{4}Be + ^{1}_{0}n$ the bombarding particle Z is deutrons.
9. A nucleus with mass defect of 0.08181 amu, the binding energy is 0.08181 × 931 ergs.
10. $^{27}_{13}Al$ is a stable isotope while $^{29}_{13}Al$ is expected to disintegrate by β-emission.

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MATCHING TYPE QUESTIONS

Match the items of column A and column B.

A	B
1. Isobars	1. $^{65}_{29}Cu$ and $^{55}_{24}Cr$
2. Isotones	2. N_2 and CO
3. Nuclei having same isotopic number	3. $^{234}_{91}Pa$ and $^{234}_{90}Th$
4. Isosters	4. $^{3}_{1}H$ and $^{4}_{2}He$
5. Element having maximum number of stable isotops	5. $^{80}_{35}Br\ (m)$ and $^{80}_{35}Br\ (g)$
6. Nuclear isomers	6. Ac
7. Radioactive element	7. Sn.

ANSWERS/HINT

REVIEW PROBLEMS

13.1. 8.512 MeV

13.2. 2×10^{-11} kg [**Hint.** Apply $\Delta E = \Delta m \times C^2$]

13.3 8.78 MeV.

13.4. $\alpha = 8, \beta = 6$

13.5. $\alpha = 3 ; \beta = 2$

13.6. A = 214 ; Z = 83, Group = 15, isodiaphers : Ra and Rn ; Rn and Po, Po and Pb ; isobars Pb and Bi

13.7. 1.2×10^{-4} year^{-1} ; 25%

13.8. $t_{1/2} = 34$ min ; $\lambda = 2.04 \times 10^{-2}$ min^{-1}

13.9. 0.0163 mg

13.10. 1.25 g

13.11. $t_{1/2} = 33.3$ min ; $\lambda = 2.09 \times 10^{-2}$ min^{-1}

13.12. 0.0693 day^{-1}

13.13. 0.76 g

13.14. (*i*) $^{2}_{1}H$, (*ii*) γ-rays (*iii*) $^{1}_{0}n$ (*iv*) $^{2}_{1}H$

13.15. 1.69×10^{9} years

13.16. 2.25×10^{9} years

13.17. 3.71×10^{9} years

13.18. 2.97×10^{3} years

13.19. 1.6989 years

13.20. 6512 years

13.21. 7629.7 years

13.22. 4672.9 years

13.23. 11460 years

13.24. 33.7 years.

VERY SHORT-ANSWER QUESTIONS

1. $^{206}_{82}Pb$
2. γ-rays
3. Mass gets decreased by 4 a.m.u.
4. The mass number of each element of the series gives a remainder equal to 2 when divided by 4.
5. 1st order
6. A is more stable
7. deutron
8. Average life is taken to be reciprocal of disintegration constant

$$\therefore \text{Average life} = \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44\, t_{1/2}$$

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9. 1 kg to 100 kg. **10.** 5 days **11.** $^{228}_{90}Th$.

12. Bacqueral **18.** Mean life time $= \frac{1}{\lambda} = \frac{t_{1/2}}{0.693} = 1.44\ t_{1/2}$.

DESCRIPTIVE QUESTIONS

30. (*i*) $^{254}_{102}No$ (*ii*) $^{209}_{83}Bi$ (*iii*) $^{2}_{1}H$ (*iv*) $^{1}_{1}H$

35. (*i*) $^{24}_{11}Na$ (*ii*) $^{1}_{0}n$ (*iii*) $^{240}_{94}Pu$ (*iv*) $5^{1}_{0}n$ (*v*) $^{246}_{99}Es$, $6^{1}_{0}n$

12. (*a*) and (*d*)

NUMERICAL PROBLEMS

47. 16800 cm^3

48. [**Hint.** The nuclear reaction is $^{235}_{92}U + ^{1}_{0}n \longrightarrow ^{98}_{42}Mo + ^{136}_{54}Xe + 4\ ^{0}_{-1}e + 2^{1}_{0}n$] **Ans.** $^{0}_{-1}e$, $^{1}_{0}n$, 207.72 MeV

49. [**Hint.** Calculate mass of $^{40}_{20}Ca$ = Mass of 20 H-atoms + Mass of 20 $^{1}_{0}n$

Mass of 20 H-atoms is equal to mass of 20 electrons and 20 protons.] **Ans.** 342.06 MeV

50. 12.33% **51.** 2.486×10^{12} J mol^{-1}

52. [**Hint.** Moles of helium collected = 5×10^{-4} mol

$N_0 = 10$ mol

$N_t = (10 - 5 \times 10^{-4})$ mol.] **Ans.** 6.584 hr.

MULTIPLE CHOICE QUESTIONS

1. (*a*)	**2.** (*c*)	**3.** (*c*)	**4.** (*a*)	**5.** (*b*)	**6.** (*b*)
7. (*c*)	**8.** (*c*)	**9.** (*b*)	**10.** (*b*)	**11.** (*d*)	**12.** (*a*)
13. (*c*)	**14.** (*c*)	**15.** (*d*)	**16.** (*d*)	**17.** (*d*)	**18.** (*a*)
19. (*a*)	**20.** (*d*)	**21.** (*b*)	**22.** (*b*)	**23.** (*d*)	**24.** (*a*)
25. (*d*)					

FILL IN THE BLANKS

1. γ-rays **2.** 6 and 4 **3.** $^{1}_{0}n$

4. isotones **5.** isobars **6.** $^{1}_{0}n$

7. $^{1}_{0}n$ **8.** $^{0}_{+1}e$ **9.** iostope

10. 93 to 104 **11.** 13 min-20 sec. **12.** Nuclear fusion.

TRUE/FALSE STATEMENTS

1. True	**2.** False	**3.** False	**4.** False	**5.** True	**6.** False
7. True	**8.** False	**9.** False	**10** True		

MATCHING TYPE QUESTIONS

1—3 ; 2—4 ; 3—1 ; 4—2 ; 5—7 ; 6—5 ; 7—6

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14

Synthetic and Natural Polymers

LEARNING OBJECTIVES

In this Unit, we shall learn

- *Classification of polymers ;*
- *Natural and synthetic polymers (with stress on their general methods of preparation) ;*
- *Important uses of the following polymers. Teflon, PVC, Nylon-66, Terylene and Synthetic rubber.*

Polymers are the chief products of modern chemical industry. The materials made of polymers find multifarious uses in all walks of our life. They have influenced our day to day life to such an extent that it is impossible to get through the day without using a material based on polymers. Common examples of these include plastic dishes, cups, non-sticking pans, automobile tyres and seat covers, plastic bags, rain coats, plastic pipes and fitting, radio and TV cabinets, wide range of synthetic fibres for clothing, synthetic glues, flooring materials and materials for biomedical and surgical operations. In this unit we shall concentrate on the chemistry and uses of some synthetic organic polymers.

14.1. MONOMERS AND POLYMERS

The word **polymers** implies "many parts" (Greek : *poly* means *many* and *merors* means *parts*). ***A polymer is a compound of high molecular mass formed by the combination of large number of small molecules.*** The small molecules which constitute the *repeating units* in a polymer are called **monomer units.** The process by which the monomers are transformed into polymer is called **polymerisation.** For example, polyethylene is a polymer which is obtained by the polymerisation of ethylene. The ethylene molecules are referred to as monomer units.

$$\underset{\text{Ethylene}}{n\,CH_2 = CH_2} \longrightarrow \underset{\text{Polyethylene}}{(-CH_2 - CH_2-)_n}$$

As polymers are *single, giant molecules, i.e.*, big size molecules, they are also called **macromolecules.**

It may be noted that the polymer formed from one kind of monomers is called **homopolymer** while polymer formed from more than one kind of monomer units is called **copolymer** or **mixed polymer.** For example, *polyethylene* is an example of homopolymer whereas *Buna-S* rubber which is formed from 1, 3-butadiene ($CH_2 = CH—CH = CH_2$) and styrene ($C_6H_5CH = CH_2$) is an example of copolymer.

14.2. CLASSIFICATION OF POLYMERS

Polymers are classified in a number of ways depending upon one criterion or the other as described below.

14.2.1. Classification Based upon Origin or Source

On the basis of source or origin, the polymers are classified into two types :

Natural polymers and *Synthetic polymers.*

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1. Natural polymers. *Polymers found in nature, mostly in plants* and *animal sources*, are called **natural polymers.** A few examples are :

(*a*) **Polysaccharides.** Starch and cellulose are very common examples of polysaccharides. They are the polymers of glucose. Starch is a chief food reserve of plants while cellulose is chief structural material of plants.

(*b*) **Proteins.** These are the polymers of α-amino acids. They are building blocks of animal cells. They constitute indespensable part of our food. Wool, natural silk, leather, etc., are proteins.

(*c*) **Nucleic acids.** These are the polymers of various *nucleotides.* RNA and DNA are common examples.

(*d*) **Natural rubber.** Substance obtained from latex is a polymer of 2-methyl-1, 3-butadiene (*isoprene*).

It may be noted that polymers like polysaccharides, nucleic acids, proteins, etc., which control various life processes in plants and animals are also called **biopolymers.**

2. Synthetic polymers. The polymers which are prepared in the laboratory are referred to as **synthetic polymers** or man-made polymers. Some examples of the synthetic polymers are *polyethylene, polystyrene, synthetic rubber, nylon, PVC, bakelite teflon, orlon,* etc.

14.2.2. Classification Based on Structure

This classification of polymers is based upon how the monomeric units are linked together. Based on their structure, the polymers are classified as :

Linear polymers,

Branched chain polymers, and

Cross-linked polymers.

1. Linear polymers. These are the polymers in which monomeric units are linked together to form long straight chains. The polymeric chains are stacked over the another to give a well packed structure.

As a result of close packing, such polymers have *high densities, high tensile strength* and *high melting points.* Common example of such type of polymers are *polyethylene, nylons* and *polyesters.*

2. Branched chain polymers. In this type of polymers, the monomeric units are linked to constitute. long chains (called the *main-chain*). There are side chains of different lengths which constitute branches.

Branched chain polymers are irregularly packed and thus, they have *low density, lower tensile strength* and *lower melting points* as compared to linear polymers. Amylopectin and glycogen are common examples of this type.

3. Cross-linked polymers. In this type of polymers, the monomeric units are linked together to constitute a three dimensional network. The links involved are called cross links. Cross-linked polymers are *hard, rigid* and *brittle* because of their network structure. Common examples of this type of polymers are *bakelite, melamine formaldehyde resin,* etc.

The linear, branched chain and cross-linked polymers, have been shown in Fig. 14.1.

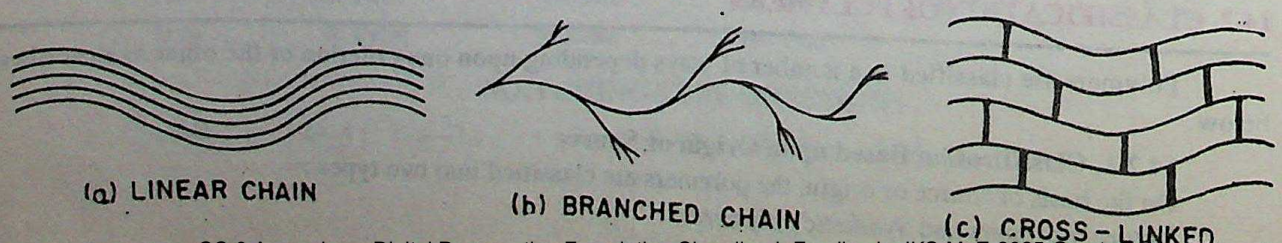

Fig. 14.1

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14.2.3. Classification based upon Synthesis

Depending upon the mode of synthesis, the polymers are classified as :

Addition polymers, and *Condensation polymers.*

1. Addition polymers. When the monomer units are repeatedly added to form long chains without the elimination of any by-product molecules, the product formed is called *addition polymer* and the process involved is called *addition polymerisation.* The monomer units are unsaturated compounds and are usually the derivatives of alkenes. The molecular formula and hence the molecular mass of the addition polymer is an *integral multiple* of that of the monomer units. Some examples of addition polymerisation are :

(*i*) $$\underset{\text{Ethylene}}{nCH_2 = CH_2} \longrightarrow \underset{\text{Polyethylene or polyethene}}{(-CH_2-CH_2-)_n}$$

(*ii*) $$\underset{\text{Propylene}}{nCH_2 = CH(CH_3)} \longrightarrow \underset{\text{Polypropylene}}{(-CH_2-CH(CH_3)-)_n}$$

(*iii*) $$\underset{\text{Acrylonitrile}}{nCH_2 = CH(CN)} \longrightarrow \underset{\text{Orlon}}{(-CH_2-CH(CN)-)_n}$$

(*iv*) $$\underset{\text{Vinyl chloride}}{nCH_2 = CH(Cl)} \longrightarrow \underset{\text{Poly vinyl chloride (PVC)}}{(-CH_2-CH(Cl)-)_n}$$

2. Condensation polymers. In this type of polymers, the monomers react together with the elimination of a simple molecules like H_2O, ROH or NH_3, etc. The reaction is called condensation and the product formed is called **condensation polymer.**

As the process involves the elimination of by-product molecules, the molecular mass of the polymer is not the integral multiple of the monomer units. For examples, *nylon-66** is a condensation polymer of hexamethylene diamine and adipic acid.

$$\underset{\text{Hexamethylene diamine}}{n\,H_2N-(CH_2)_6-NH_2} + \underset{\text{Adipic acid}}{n\,HOOC-(CH_2)_4-COOH}$$

$$\longrightarrow \underset{\text{Nylon-66}}{(-\overset{H}{\overset{|}{N}}-(CH_2)_6-\overset{H}{\overset{|}{N}}-\underset{\underset{O}{\|}}{C}-(CH_2)_4-\underset{\underset{O}{\|}}{C}-)_n} + 2nH_2O$$

Some other examples of condensation polymers are :

Dacron (polyester). A polymer of *ethylene glycol* and *terepthalic acid.*

Bakelite. A polymer of *phenol* and *formaldehyde.*

Chain Growth and Step Growth Polymers

Many a times, it becomes difficult to find out whether the polymerisation has occurred through condensation or through addition. Therefore, a more rational classification has recently been proposed

*The name 'nylon-66' refers to the fact that the polyamide is made from dicarboxylic acid of 6-carbon atoms and diamine of 6-carbon atoms.

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according to the *mechanism of combination of monomer units*. The two types of polymers according to this system are

Chain growth polymers, and *Step growth polymers.*

1. Chain Growth Polymers. Chain growth polymerisation is a process of successive addition of monomer units to the growing chain by a chain mechanism. The monomer unit gets converted to some active intermediate species by a small amount of *initiator* such as *organic peroxide* or *an acid* or *a base.* Depending upon the conditions, the intermediate species may be free radical or an ion, and it reacts with other monomer unit to form still bigger intermediate species. The monomer units are, thus, successively added to intermediate species by a chain process. Let us illustrate the chain growth polymerisation of ethene involving free radical initiation.

(*i*) $$\textit{Initiator} \xrightarrow[\text{up}]{\text{Split}} \underset{\text{Free radicals}}{\dot{A}}$$

(*ii*) $$\dot{A} + \underset{\text{Monomer}}{CH_2 = CH_2} \longrightarrow \underset{\text{Intermediate species}}{A—\dot{C}H_2—\dot{C}H_2}$$

(*iii*) $$A—\dot{C}H_2—\dot{C}H_2 + \underset{\text{Monomer}}{CH_2 = CH_2} \longrightarrow \underset{\text{Bigger intermediate species}}{A—CH_2—CH_2—CH_2—\dot{C}H_2}$$

A *chain propagation* is, thus, set up which results in the growth of the chain by repeated addition of monomer units. The polymers formed by chain growth polymerisation are called **chain growth polymers.** Addition polymers are formed, generally by this process.

Some examples of chain growth polymers are :

Polyethylene, polypropylene, teflon, polyisoprene, etc.

2. Step-Growth Polymers. As the name suggests, the step growth polymerisation involves stepwise intermolecular condensation taking place through a series of independent reactions. Each reaction involves a condensation process involving the loss of a simple molecule like NH_3, H_2O, HCl, etc. This type of polymerisation occurs if the monomer molecules have more than one similar or dissimilar functional groups. Let us illustrate the step growth polymerisation in the simplest way starting with two monomers **A** and **B**.

$$\underset{\text{Monomer}}{A + B} \xrightarrow[\text{Step I}]{\text{Condense}} A—B$$

$$A—B + A \xrightarrow[\text{Step II}]{\text{Condense}} A—B—A$$

$$A—B—A + B \xrightarrow[\text{Step III}]{} A—B—A—B$$

The stepwise process of chain growth, thus goes on. The stepwise growth can also take place in another manner.

$$A + B \xrightarrow[\text{Condense}]{\text{Step I}} A—B$$

$$A—B \xrightarrow[\text{Step II}]{A—B} A—B—A—B \ldots\ldots \underset{\text{Polymer}}{(A—B)_n}$$

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The polymers formed by step growth polymerisation are called **step growth polymers.** The condensation polymers like *dacron, nylon, backelite* are formed by this type of polymerisation.

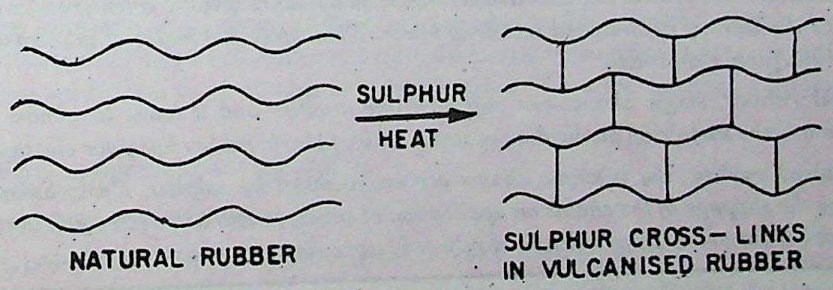
14.2.4. Classification Based on Interparticle Forces

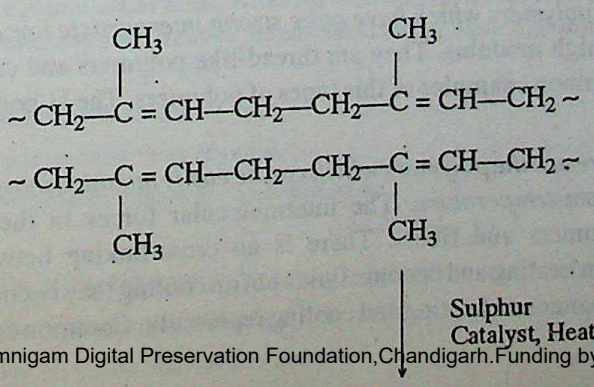
The mechanical properties of polymers such as tensile strength, toughness, elasticity, etc., depend upon intermolecular forces like van der Waal's forces and hydrogen bonds existing in the macromolecules. Although these intermolecular forces are present in simple molecules also, but their effect is less significant in them as compared to that in macromolecules. It is because of the fact, that in polymers there is a combined effect of these forces all along the long chains. Obviously, longer the chain, more intense is the effect of intermolecular forces.

Polymers have been classified into the **four** categories on the basis of the magnitude of intermolecular forces present in them. These are :

Elastomers, Fibers, Thermoplastics, and *Thermosetting polymers.*

1. Elastomers. These are the *polymers having elastic character.* The polymer chains in such type of polymers are held together by weakest intermolecular forces. These forces permit the polymer to be stretched under stress but they regain their former shape when the stress is relieved. Rubber, synthetic or natural, is the best known elastomer. The elasticity of such polymers can be further modified by introducing few *cross-links* between the chains. For example, natural rubber, a gummy material, has a poor elasticity. It is a polymer of isoprene ($CH_2 = C(CH_3) — CH = CH_2$). In 1839, Charle's Goodyear discovered that heating gummy rubber with sulphur produced a material which was no longer sticky but had modified elasticity. Such a material was called **Vulcanized rubber.** Valcanization of natural rubber introduces *sulphur cross-links* which help to allign the polymer chains in such a way so that the material does not undergo a permanent change when stretched, but springs back to original shape and size after the stress is removed as shown in Fig. 14.2. The cross-links of sulphur in isoprene units in vulcanised rubber have been shown below :





Natural rubber

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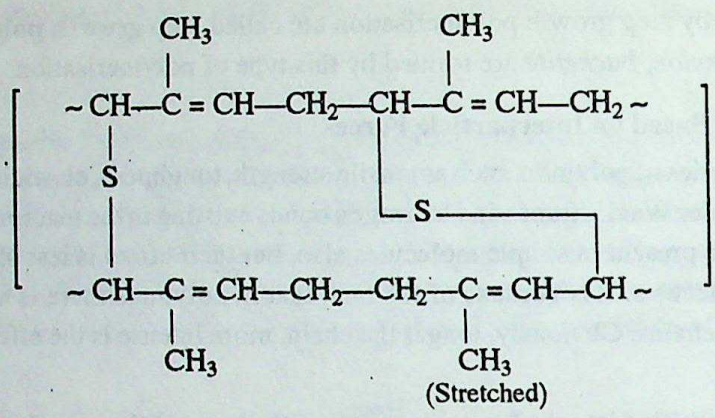

Vulcanised rubber containing cross-links of sulphur

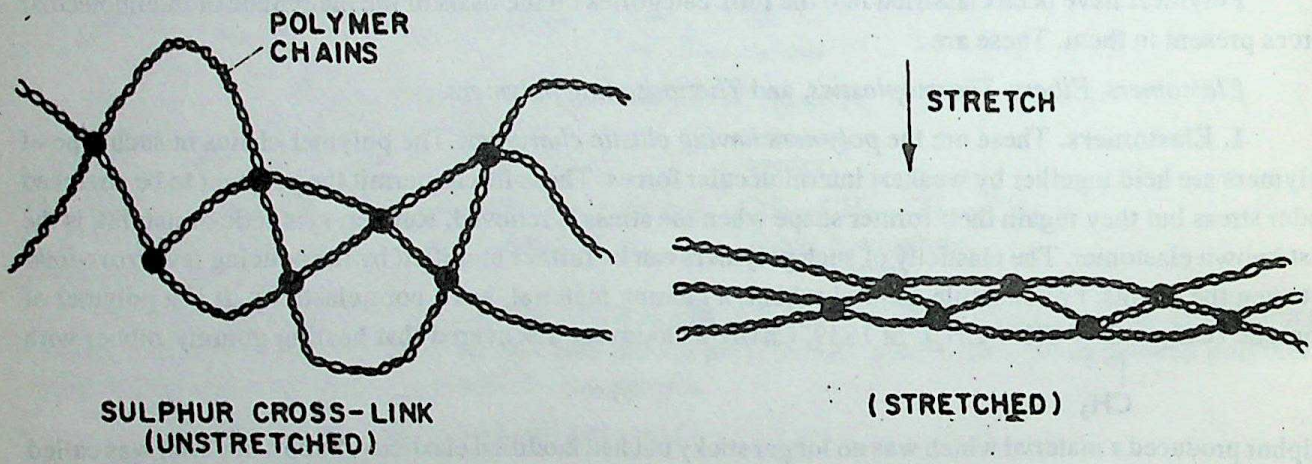

Fig. 14.2. Stretched vulcanised rubber.

- **Elasticity of Rubber.** *It is a special physical property of rubber that results from the structure of the polymer. Long flexible macromolecules tend to coil up in a random way. The molecules are uncoiled when the material is stretched. The uncoiled arrangement has more specific geometry than the random coil. Hence the entropy of stretched rubber is lower. When stretched material is released, entropy increases and rubber contracts.*
- In **natural rubber,** *single chains can slip past one another and it leads to almost permanent deformation of the sample on application of stress. Thus, natural rubber has poor elasticity.*
- In **vulcanised rubber,** *the isoprene chains are cross-linked by sulphur. Cross-linking helps in preventing the slippage of the chains on application of stress. It also helps to region the shape after the removal of the stress. Thus, vulcanised rubber is more elastic than natural rubber.*

2. Fibers. *These are the polymers which have quite strong interparticle forces such as H-bonds.* They have high tensile strength and high modulus. They are thread-like polymers and can be woven into fabrics. Nylon, dacron silk are some common examples of this types of polymers. The H-bonds in nylon-66 have been shown in Fig. 14.3.

3. Thermoplastics. *There are the polymers which can be easily moulded into desired shapes by heating and subsequent cooling to room-temperature.* The intermolecular forces in thermoplastic polymers are intermediate to those of elastomers and fibers. There is no cross-linking between the chains. In fact, thermoplastic polymers soften on heating and become fluids but on cooling they become hard. They are capable of undergoing such reversible changes on heating and cooling repeatedly. Common examples of thermoplastics are *polyethene* and *polystyrene*.

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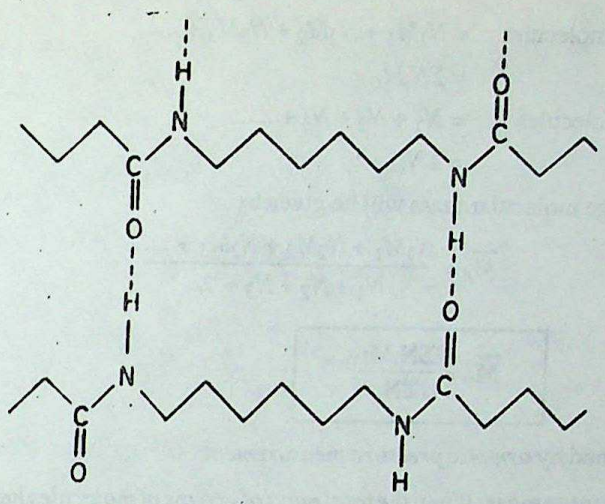

Fig. 14.3. H-Bonding in nylon-66.

Plasticizers. Certain plastics do not soften to workable extent on heating. Such plastics can be easily softened by the addition of some organic compounds which are known as **plasticizers.** For examples, polyvinyl chloride (PVC) is extremely stiff even while hot. However, addition of di-*n*-butylphthalate, a plasticizer, makes it soft and workable.

4. Thermosetting polymers. These are the *polymers which become hard and infusible on heating.* They are normally made from *semi-fluid substances* with low molecular masses, by heating in a mould. Heating results in *excessive cross-linking between the chains* forming three dimensional network of bonds as a consequence of which a *non-fusible* and *insoluble* hard material is produced. Bakelite is a common example of thermosetting polymer.

In short, a **thermoplastic material** *can be remelted time and again without change, while a* **thermosetting material** *undergoes a permanent change upon melting and thereafter sets to a solid which cannot be remelted.*

14.3. MOLECULAR MASS OF POLYMERS

During the formation of polymers, different macromolecules have different degree of polymerization *i.e.*, they have different chain lengths. Thus, the molecular masses of the individual macromolecules in a particular sample of polymer are different. Hence, an average value of molecular mass is taken. There are two types of average molecular masses of poymers.

(*i*) Number-average molecular mass ($\overline{M}_n$)

(*ii*) Mass-average molecular mass ($\overline{M}_w$)

The two types of molecular masses are defined and calculated as follows :

(*i*) **Number-average molecular mass.** *When the total mass of all the molecules of a sample is divided by the total number of molecules, the result obtained is called the number-average molecular mass.* For example, suppose in a particular sample

N_1 molecules have molecular mass M_1 each.

N_2 molecules have molecular mass M_2 each.

N_3 molecules have molecular mass M_3 each and so on.

Then, we have

Total mass of all the N_1 molecules = N_1M_1.

Total mass of all the N_2 molecules = N_2M_2.

Total mass of all the N_3 molecules = N_3M_3 and so on.

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$\therefore$ Total mass of all the molecules $= N_1M_1 + N_2M_2 + N_3M_3 + ...$

$= \Sigma N_iM_i$

Total number of all the molecules $= N_1 + N_2 + N_3 + ...$

$= \Sigma N_i$

Hence the number-average molecular mass will be given by

$$\overline{M}_n = \frac{N_1M_1 + N_2M_2 + N_3M_3 + ...}{N_1 + N_2 + N_3 + ...}$$

or

$$\boxed{\overline{M}_n = \frac{\Sigma N_iM_i}{\Sigma N_i}}$$

$\overline{M}_n$ is generally determined by *osmotic pressure measurement.*

(*ii*) **Mass-average molecular mass.** *When the total mass of groups of molecules having different molecular masses are multiplied with their respective molecular masses, the products are added and the sum is divided by the total mass of all the molecules, the result obtained is called the mass-average molecular mass.* Supposing, as before that N_1, N_2, N_3, etc., molecules have molecular mass M_1, M_2, M_3 etc. respectively.

Total mass of N_1 molecules $= N_1M_1$

Total mass of N_2 molecules $= N_2M_2$

Total mass of N_3 molecules $= N_3M_3$ and so on.

The products with their respective molecular masses will be $(N_1M_1 \times M_1)$, $(N_2M_2 \times M_2)$, $(N_3M_3 \times M_3)$, etc., *i.e.*, $N_1M_1^2, N_2M_2^2, N_3M_3^2$, etc.

Sum of the products $= N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + ...$

$= \Sigma N_iM_i^2$

Total mass of all the molecules $= N_1M_1 + N_2M_2 + N_3M_3 + ...$

$= \Sigma N_iM_i$

Hence the mass-average molecular mass is given by

$$\overline{M}_w = \frac{N_1M_1^2 + N_2M_2^2 + N_3M_3^2 + ...}{N_1M_1 + N_2M_2 + N_3M_3 + ...}$$

or

$$\boxed{\overline{M}_w = \frac{\Sigma N_iM_i^2}{\Sigma N_iM_i}}$$

$\overline{M}_w$ is generally determined by techniques like *ultra centrifugation* or *sedimentation.*

Poly Dispersity Index (PDI). In general, we have two different types of polymeric substance

(*i*) Polymers whose molecules have same or narrow range of molecular masses. Such polymers are said to be **monodisperse.**

(*ii*) Polymers which have wide range of molecular masses. Such polymers are called **polydisperse.**

In order to have an idea about the homogeneity of a polymer we define the term called ***polydispersity index.*** It is the ratio of the mass average molecular mass to the number average molecular mass.

$$PDI = \overline{M}_w/\overline{M}_n$$

For natural polymers, *PDI* is usually equal to one which means that they are monodisperse. Such polymers are more homogeneous. Synthetic polymers on the contrary generally have $PDI > 1$ which means that they are less homogeneous.

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Example 14.1. *In a particular sample of a polymer, 100 molecules have molecular mass 10^3 each, 200 molecules have molecular mass 10^4 each and 200 molecules have molecular mass 10^5 each. Calculate the number-average and mass average molecular mass.*

Solution.

$$\overline{M}_n = \frac{100 \times 10^3 + 200 \times 10^4 + 200 \times 10^5}{100 + 200 + 200}$$

$$= \frac{10^5 (1 + 20 + 200)}{500} = 4.4 \times 10^4 = 44{,}000$$

$$\overline{M}_w = \frac{100 \times (10^3)^2 + 200 \times (10^4)^2 + 200 \times (10^5)^2}{100 \times 10^3 + 200 \times 10^4 + 200 \times 10^5}$$

$$= \frac{10^8 (1 + 200 + 20000)}{10^5 (1 + 20 + 200)} = \frac{10^3 \times 20201}{221} = 91{,}000.$$

It may be noted that $\overline{M}_w > \overline{M}_n$.

Problem 14.1. In a polymer sample, 30% molecules have molecular mass 20,000, 40% have molecular mass 30,000 and rest 30% have 60,000. Calculate $\overline{M}_w$ and $\overline{M}_n$.

Hint.

$$\overline{M}_n = \frac{(30 \times 20000) + (40 \times 30000) + (30 + 60000)}{30 + 40 + 30} = 36{,}000$$

$$\overline{M}_w = \frac{30(20000)^2 + 40(30000)^2 + 30(60000)^2}{30 \times 20000 + 40 \times 30000 + 30 \times 40000} = 43333.$$

REVIEW QUESTIONS

14.1. To which category does each of these polymers belong ; natural or synthetic ?

(*i*) Starch, (*ii*) Nylon-66 (*iii*) Cellulose (*iv*) PVC.

14.2. Each of the following is used for polymerisation, pick up the type of polymer they will form

(*i*) $CH_2 = CH—CH_3$ (*ii*) C_6H_5OH and NH_2CONH_2

(*iii*) $CH_2 = CHCl$ (*iv*) $C_6H_5CH = CH_2$

14.3. In which type of polymers the interparticle forces are strongest ?

(*i*) Linear (*ii*) Branched Chain

14.4. What type of structure is possessed by thermosetting polymers ?

14.5. To which category of polymers does vulcanised rubber belong ?

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14.4. SOME COMMERCIALLY IMPORTANT POLYMERS

In this section, we shall study the important uses of some addition as well as condensation polymers.

14.4.1. Addition Polymers

As described earlier, here the monomer units are alkenes or their derivatives. Some examples are discussed below.

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A. Polyolefins. These are the polymers derived from unsaturated hydrocarbons such as alkenes. Some examples along with their uses are being discussed below :

1. Polyethylene or Polyethene

The *monomer* units are **ethylene molecules.** It is manufactured by heating ethylene to 465—485 K under pressure in the presence of 0.03 to 0.1% of oxygen.

$$n\,CH_2 = CH_2 \xrightarrow[\text{Traces of oxygen}]{465\text{—}485\text{ K, }15000\text{ atm}} \underset{\text{Polyethene}}{(-CH_2-CH_2-)_n}$$

Characteristics and uses. It is a white transluscent material. Low density polyethene is flexible but high density polyethene is harder, tough and chemically inert. It is frequently used in :

coats, milk cartons, bread wrappers, carry bags, toys and *electrical insulations.*

2. Polypropylene

The monomer units are **propylene molecules.** It is generally manufactured by passing propylene through *n-hexane* (inert solvent) containing Ziegler-Natta catalyst (a mixture of triethyl aluminium and titanium chloride).

$$\underset{\text{Propylene}}{n\,CH(CH_3) = CH_2} \xrightarrow[TiCl_3]{Al(C_2H_5)_3} \underset{\text{Polypropylene}}{(-CH(CH_3)-CH_2-)_n}$$

Characteristics and uses. It is harder, stronger and lighter than polyethene. It is used in :

packing of textile material and food, liners of bags, gramophone records and *ropes.*

3. Polystyrene

The monomer units are **styrene molecules.** It is prepared by free radical polymerisation of styrene in the presence of benzoyl peroxide.

$$\underset{\text{Styrene}}{n\,CH(C_6H_5) = CH_2} \xrightarrow{(C_6H_5CO)_2O} \underset{\text{Polystyrene}}{(-CH(C_6H_5)-CH_2-)_n}$$

Characteristics and uses. It is a white thermoplastic material which is transparent and floats on water. It is used for making *toys, combs, model construction kits, ceiling tiles, packing for delicate articles* and *lining material for refrigerators* and *TV cabinets.*

Polystyrene is sold under the name *styrofoam* or *styron.*

B. Polyhaloolefines. This type of polymers are derived from halogen substituted olefins, *i.e.*, haloalkenes. Some common examples are :

1. Teflon or Polytetrafluoro ethylene (PTFE)

The monomer unit is **Tetrafluoroethylene molecules.** It is prepared by heating tetrafluoroethylene under pressure in the presence of ammonium peroxosulphate $[(NH_4)_2S_2O_8]$.

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$$\underset{\text{Tetrafluoroethylene}}{n\,CF_2 = CF_2} \xrightarrow[\text{Heat, pressure}]{(NH_4)_2S_2O_8} \underset{\text{Teflon}}{(-CF_2-CF_2-)_n}$$

Characteristics and uses. It is a very tough material and is resistant towards heat, action of acids or bases. It is bad conductor of electricity. It is used in :

coating utensils to make them non-sticking, making seals and gaskets which can withstand high pressures, insulations for high frequency electrical installations.

2. Poly monochlorotrifluoro ethylene (PCTFE)

The monomer unit are **chlorotrifluoro ethylene** molecules. It is prepared by the polymerisation of monochlorotrifluoro ethylene

$$\underset{\text{Chlorotrifluoro ethylene}}{n\,ClFC = CF_2} \longrightarrow \underset{\text{PCTFE}}{(-ClFC-CF_2-)_n}$$

The properties of PCTFE are similar to teflon. However, this is relatively less resistance to heat and chemicals.

3. Polyvinylchloride (PVC)

The monomer units are **vinyl chloride** molecules. It is prepared by heating vinyl chloride in an inert solvent in the presence of dibenzoyl peroxide.

$$\underset{\text{Vinyl chloride}}{n\,CH_2 = \underset{\underset{Cl}{|}}{CH}} \xrightarrow{\text{Dibenzoyl peroxide}} \underset{\text{PVC}}{(-CH_2-\underset{\underset{Cl}{|}}{CH}-)_n}$$

Characteristics and uses. PVC is a hard horny material. However, it can be made to acquire any degree of pliability by the addition of a *plasticizer*. It is resistant to chemicals as well as heat. It is used for making :

rain coats, hand bags, toys, hosepipes, gramophone records, electrical insulations and *floor covering.*

C. Polydienes. Two of the commercially important polymers of *dienes* are : *neoprene* and *Buna*-S.

1. Neoprene

This is synthetic rubber which resembles natural rubber in its properties. It is obtained by polymerisation of **chloroprene** (2-chloro-1, 3-butadiene) in the presence of potassium persulphate.

$$\underset{\text{Chloroprene}}{n\,CH_2 = \underset{\underset{Cl}{|}}{C}-CH = CH_2} \xrightarrow{K_2S_2O_8} \underset{\text{Neoprene}}{(-CH_2-\underset{\underset{Cl}{|}}{C} = CH-CH_2-)_n}$$

Characteristics and uses. Neoprene is superior to natural rubber in its stability to aerial oxidation and also in its resistance to oils and other solvents. It is generally used for making :

hoses, shoeheels, stoppers and *belts.*

2. Buna-S

It is a copolymer of *1, 3-butadiene* and *styrene*. It is obtained by the polymerisation of butadiene and styrene in the ratio of 3 : 1 in the presence of sodium. It is also known as *styrene butadiene rubber* (**SBR**).

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$$\underset{\text{Butadiene}}{n\,CH_2=CH-CH=CH_2} + \underset{\text{Styrene}}{n\,C_6H_5CH_5=CH_2} \xrightarrow[\text{Heat}]{\text{Na,}} \underset{\text{Buna-S}}{\left(-CH_2-CH=CH-CH_2-\underset{\underset{C_6H_5}{|}}{CH}-CH_2-\right)_n}$$

In Buna-S, *Bu* stands for butadiene ; *na* for sodium which is polymerising agent and S stands for *styrene*.

Characteristics and uses. SBR has slightly less tensile strength than natural rubber. It is used in the manufacture of :

automobile tyres, rubber soles, belts, hoses, etc.

D. Polyacrylates. Polymers of this class are obtained from the esters of acrylic acid ($CH_2 = CHCOOH$). Some common examples are being discussed as follows in tabular form.

	Formula of monomer	*Polymer*	*Characteristics*	*Uses*
1.	$CH_2=C(CH_3)-COOCH_3$ Methyl methacrylate	$\left(-CH_2-C(CH_3)(COOCH_3)-\right)_n$ Polymethyl methacrylate (PMMA) [**Commercial names** of (PMMA) are *Lucite, Plexiglass, Acrylite, Ferspex*]	Hard transparent, high optical clarity. It is capable of acquiring different colours and tints.	Used in : *lenses, transparent objects, domes and skylights, aircraft windows, protective coatings, plastic jewellery*, etc.
2.	$CH_2=CH-COOC_2H_5$ Ethyl acrylate	$\left(-CH_2-CH(COOC_2H_5)-\right)_n$ Polyethyl acrylate	Tough and rubbery polymer.	Almost similar to PMMA.
3.	$CH_2=CH-CN$ Acrylonitrile	$\left(-CH_2-CH(CN)-\right)_n$ Polyacrylo nitrile (PAN) or *Acrilan* or *Orlon*	Hard, horny and high melting material.	Used in : preparing *cloth, carpets* and *blankets*.

All these polymerisation reactions are carried out in the presence of peroxides.

14.4.2. Condensation Polymers

As pointed out earlier, these type of polymers are formed as a result of condensation reaction between monomer units. Some common examples are being discussed below :

A. Polyesters. These are the polymers having ester linkage ($-\overset{O}{\overset{\|}{C}}-O-\overset{O}{\overset{\|}{C}}-$). Some examples are :

1. Terelene. It is a polymer obtained by the condensation reaction between *ethylene glycol* and *terephthalic acid*.

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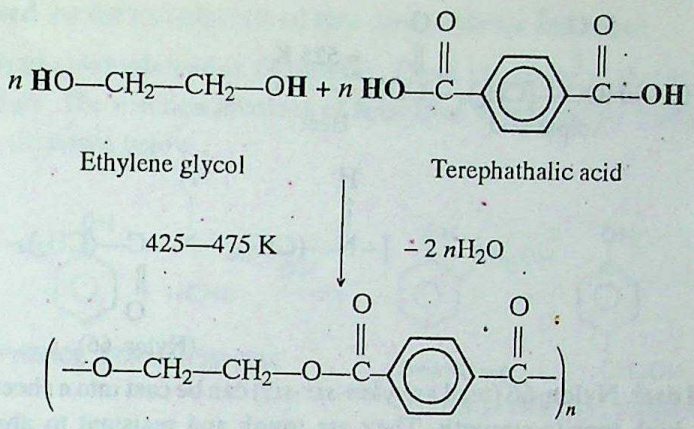
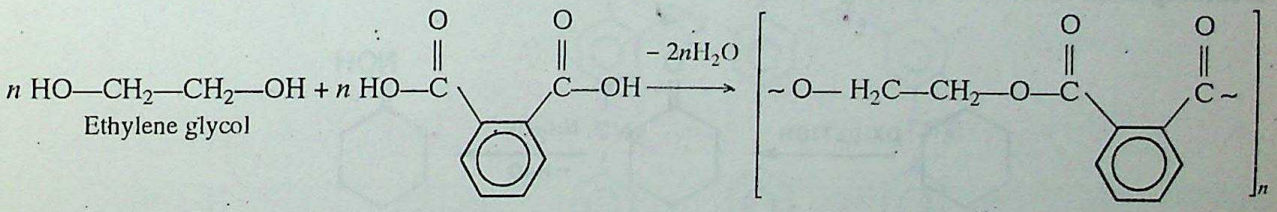


Poly (ethylene glycol terephthalic) or *Terelene*

Characteristics and uses. Terelene is resistant to the action of chemical and biological substances and also to abrasion. It has a low moisture absorbing power. As such it is widely used in making wash and wear fabrics. The polyester textile fibers made from the polymer are marketed under the trade name *terelene* or *dacron.*

It is used as a blend with cotton and wool in clothing. It is also used in *seat belts* and *sails.* The polymer is also used as **mylar** in the preparation of *films, magnetic recording tapes* and for *packing forzen food.* Dacron (and teflon) tubes are *good substitutes for human blood vessels in heart by-pass operations.*

2. Glyptal or Alkyd resin. Glyptal is a general name of all polymers obtained by condensation of *di-basic acids,* and *polyhydric alcohols.* The simplest glyptal is *poly* (*ethylene glycol phthalate*) which is obtained by the condensation of *ethylene glycol* and *phthalic acid.*



Phthalic acid Poly (ethylene glycol phthalate)

Characteristics and uses. These are three dimensional cross-linked polymers. Poly (ethylene glycol phthalate) dissolves in suitable solvents and the solution on evaporation leaves a tough and non-flexible film. Thus, it is used in :

adherant paints, lacquers and *building materials* like *asbestos and cement.*

B.Polyamides. Such polymers have amide linkage ($\sim C(=O)-NH\sim$) in the chain and are called polyamides.

Some common examples are :

1. Nylon-6,6. It is a polymer of *adipic acid* (1, 6-hexanedioic acid) and *hexamethylene diamine* (1, 6-diaminohexane)

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$$n\,H_2N{-}(CH_2)_6{-}NH_2 + n\,HOC{-}(CH_2)_4{-}COH \xrightarrow[\text{Heat}]{\approx 525\ K} [\sim N{-}(CH_2)_6{-}N(H){-}C(=O){-}(CH_2)_4{-}C(=O)\sim]_n + 2nH_2O$$

Hexa-methylene diamine; Adipic acid; (Nylon-66)

Characteristics and uses. Nylon-66 (read as *nylon-six-six*) can be cast into a sheet or fibers by spinning devices. Nylon fibers have high tensile strength. They are tough and resistant to abrasion. They are also somewhat elastic in nature. Nylon finds uses in :

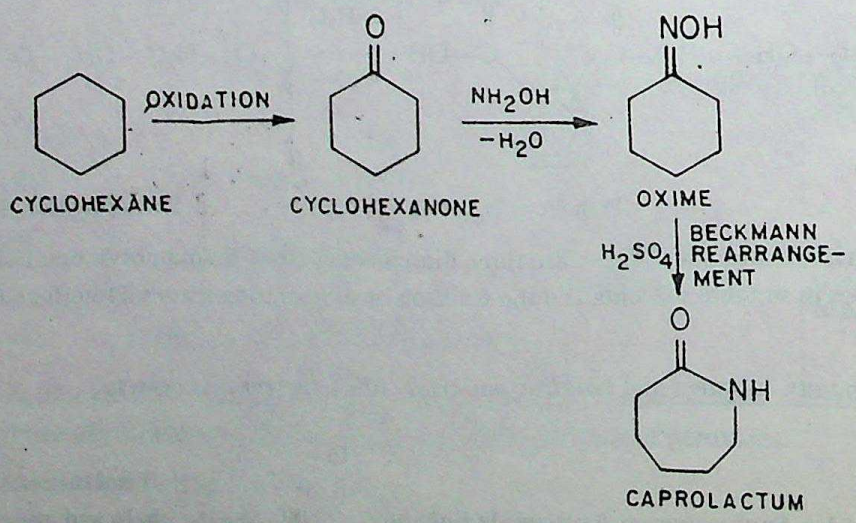
making bristels and brushes, carpets and *fabrics* in *textile industry, elastic hosiery* in the form of *crinkled nylon.*

2. Nylon 6, 10. It is a polymer of hexamethylene diamine (six carbon atoms) and sebacoyl chloride (ten carbon atoms)

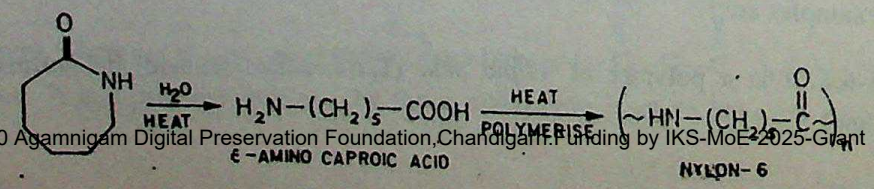
$$n\,H_2N(CH_2)_6{-}NH_2 + n\,Cl{-}C(=O)(CH_2)_8{-}C(=O){-}Cl \xrightarrow{\text{heat}} [{-}HN{-}(CH_2)_6{-}N(H){-}C(=O){-}(CH_2)_8{-}C(=O){-}]_n + 2nHCl$$

Nylon 610

3. Nylon-6. It is obtained from the monomer *caprolatum.* Caprolactum is obtained from *cyclohexane* according to the reaction sequence given below :



Caprolactum on heating with traces of water hydrolyses to *6-amino caproic acid* which on continued heating undergoes self-condensation and polymerises to give *nylon-6*.



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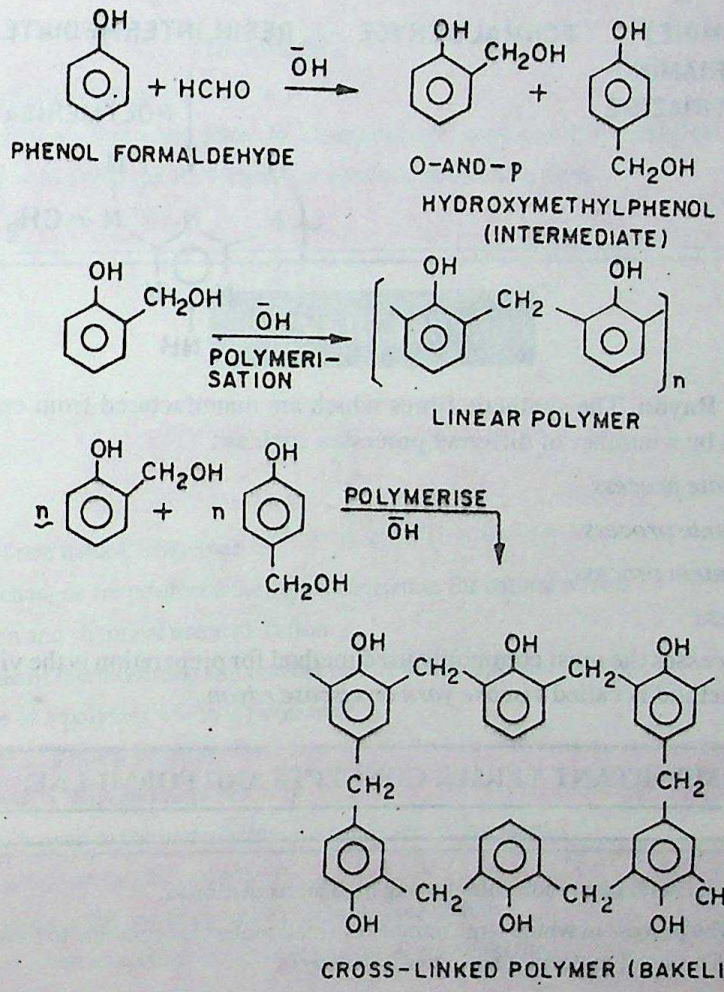
Nylon-6 is used for the manufacture of *tyre cords, fabrics* and *ropes.*

C. Phenol-Formaldehyde resins (Bakelite). These are made by the reaction of *phenol* and *formaldehyde* in basic medium. The reaction involves of formation of methylene bridges in *ortho, para* or ortho as well as para position as shown below :



Characteristics and uses. Bakelite is a cross-linked thermosetting polymer. Soft bakelites with low degree of polymerization are used as *bonding glue for laminated wooden planks, in the preparation of varnishes and lacquers.*

High degree of polymerization leads to formation of hard bakelite which is used for making combs, fountain pen barrels, gramophone records, electrical goods, formica table tops and many other products. Sulphonated bakelites are used as ion-exchange resins for softening of hard water.

D. Melamine formaldehyde resin

Melamine and formaldehyde copolymerize to give another polymer.

Characteristics and uses. Malamine polymer is quite hard and is used in making plastic crockery under the trade name *melmac.* Cups, plates and other articles made from malamine polymer do not break on being dropped.

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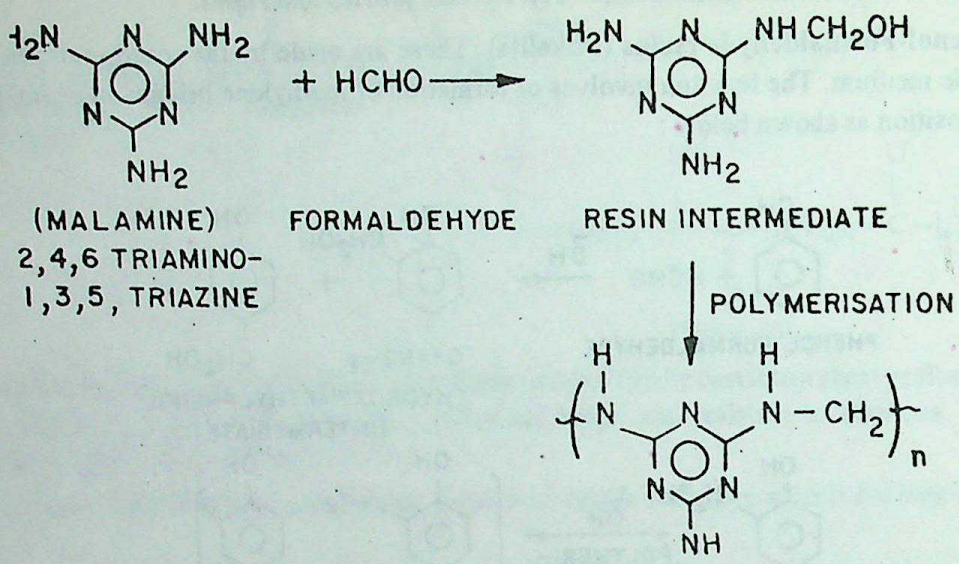

Artificial silk or Rayon. The synthetic fibres which are manufactured from cellulose are known as rayon. It is manufactured by a number of different processes such as :

(*i*) *Cellulose nitrate process*

(*ii*) *Cellulose acetate process*

(*iii*) *Cupro ammonium process*

(*iv*) *Viscose process.*

Among these processes the most commonly used method for preparation is the viscose process and the rayon obtained by this method is called *viscose yarn or viscose rayon.*

IMPORTANT TERMS, CONCEPTS AND FORMULAE

- **Polymer.** A substance with giant molecules having high molecular mass.
- **Polymerization.** The process in which large number of small molecules combine to form a giant molecule or a macromolecule. The small molecules are called *monomers.*
- **Homopolymer.** A polymer formed by combination of only one type of monomers.
- **Copolymer.** A polymer formed by combination of two or more different types of monomers.
- **Addition Polymers.** The polymers formed by combination of large number of monomers without the elimination of any smaller molecules.
- **Condensation Polymers.** During formation of such polymers, elimination of smaller molecules such as H_2O, NH_3, etc. takes place.
- **Elastomers.** In this type of polymers, the polymeric chains are held by weak intermolecular forces. For example, rubber.
- **Fibres.** These are thread like polymers having hydrogen bonds as intermolecular forces between different polymeric chains. For examples, cotton, nylon-66.
- **Thermoplastics.** These are the polymers that soften on heating and can be moulded into any shape. Intermolecular forces in them are intermediate between fibres and elastomers.

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- **Thermosetting polymers.** These polymers are very hard, infusible and have extensive cross links. For example, bakelite.
- **Isoprene.** 2-Methyl-1, 3-butadiene. Monomer of natural rubber.
- **Neoprene.** Synthetic rubber, having chloroprene as the monomeric units.
- **Poly Dispersity Index (PDI).** Ratio of mass average molecular mass ($\overline{M}_w$) and number average molecular mass ($\overline{M}_n$)

$$PDI = \overline{M}_w/\overline{M}_n$$

Homogeneous polymers have PDI close to 1.

- **Plasticizer.** A substance that when added to a thermoplastic improves its workability.
- **Caprolactum.** Starting material for Nylon-6, a synthetic polyamide fibre.
- **Wool.** A natural polyamide fibre.

EXERCISES

VERY SHORT ANSWER QUESTIONS
(1 Mark)

1. Give the name of one natural elastomer.
2. What structural changes are produced during vulcanisation for natural rubber ?
3. Give abbreviation and chemical name of Teflon.
4. Give one example of thermosetting and another one of thermosplastic polymer.
5. Give an example of a polymer which is *polyamide.*
6. Give the example of a linear polymer.
7. Give an example of a polyester polymer.
8. Which substance is used in the manufacture magnetic recording tapes ?
9. Which polymer is known as gutta-percha ?
10. Which polymer involve the use of caprolactum in its preparation ?
11. Write the reaction between formaldehyde and phenol to give bakelite. ***(Pb.S.B. 1991)***
12. Write the monomer units of bakelite. ***(H.P.S.B. 1993)***
13. Write the monomer of teflon. Give its uses.

DESCRIPTIVE QUESTIONS
(2 or 3 Marks)

14. What is meant by the terms chain growth polymerisation and step growth polymerisation ?
15. Explain the following terms with examples :
    (*i*) Polyester ; (*ii*) Polyamide ; (*iii*) Natural polymers ; and (*iv*) Synthetic polymers.
16. Give the classification of polymers :
    (*a*) On the basis of their mode of synthesis ; and
    (*b*) On the basis of nature of forces between the macromolecules.
    Give suitable example in each case.

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17. What is a polyamide ? How is Nylon-6 synthesized ? [*A.I. CBSE (O) 1993*]
18. What is Buna-S and how is it synthesised ? (*Pb. Board 1993*)
19. How does vulcanised rubber differ from natural rubber ?
20. Define the terms :

    Thermoplastic polymers, Thermosetting polymers, Fibers, and Elastomers.
21. Give the starting material of each of the following :

    (*i*) PMMA (*ii*) PCTFE
    (*iii*) PAN (*iv*) PVC.
22. What is the difference between nylon-6 and nylon-66 ? [*CBSE (3) 1992*]
23. Give the structures of monomers of bakelite. How is it formed ? To which class, *thermosetting* or *thermoplastic* does it belong ? Give reasons.
24. Write the names and structures of the monomer of each of the following. Give one use of each of the polymers ?

    (*ii*) Terelene (*ii*) Neoprene
    (*iii*) Natural rubber (*iv*) Lucite.
25. How is the molecular mass of polymers expressed ? Give examples.
26. Write the equations for the synthesis of :

    (*i*) Glyptal (*ii*) Poly (ethyleneterephthalate)
    (*iii*) Poly acrylo nitrile (*iv*) Malamine-formaldehyde resin.
27. What do you understand by linear, branched chain and cross-linked polymers ?
28. Given examples of polymers belonging to following categories. Give their structures :

    (*i*) Polyamide (*ii*) Polyhaloolefins (*iii*) Polyolefins
    (*iv*) Polyesters (*v*) Polyacrylates.
29. Describe chain growth and step growth polymerisation. [*A.I. CBSE (O) 1990, 91*]
30. How is Nylon-66 synthesised ? [*A.I. CBSE (O) 1991*]
31. What is the difference between polyacrylates and polyester ? [*CBSE (1) 1992*]
32. What are polyolefins and polydienes ? [*CBSE (2) 1992*]
33. Define the terms (*i*) thermosetting and step-growth polymerisation. [*CBSE (4) 1992*]

    (*ii*) Thermoplastic and Elastomers. [*A.I. CBSE (O) 1992*]
34. What are polymers ? Explain the term poly dispersity index (PDI) ? (*CBSE 1992*)
35. Give the preparation and uses of PVC. [*Har. (Sc.) 1992*]
36. Give the equations for the synthesis of Nylon-6 from cyclohexane. (*Pb. S.B. 1995*)
37. Write the structure of nylon-66. What is the difference between nylon-6 and nylon-66 ? (*Pb. S.B. 1994*)
38. Write chemical equations for the synthesis of

    (*i*) Teflon (*ii*) Glyptal (*iii*) Polyvinyl chloride. (*H.P.S.B. 1994*)
39. Briefly describe the following terms giving one example of each :

    (*i*) Polyolefins (*ii*) Polyamides (*iii*) Polyesters. (*A.I. CBSE 1994*)
40. Arrange the following polymers in increasing order of their intermolecular forces. Also classify them as addition and condensation polymers. Nylon-6, Neoprene, PVC. (*A.I. CBSE 1995*)
41. Arrange the following polymers in increasing order of their intermolecular forces. Also classify them as addition and condensation polymers. Nylon-66, Buna-S, Polythene. (*CBSE 1995*)
42. Mention which of the following are addition polymers.

    (*i*) Terylene (*ii*) Nylon 66
    (*iii*) Neoprene (*iv*) Teflon. (*CBSE 1997*)

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select the correct answer from questions 1 to 20 :

1. Polymers are
   (*a*) micromolecules (*b*) macromolecules (*c*) sub-micromolecules (*d*) none of these.
2. Bakelite is
   (*a*) addition polymer (*b*) elastomer (*c*) thermoplastic (*d*) thermosetting.
3. Buna-S is
   (*a*) natural polymer (*b*) synthetic polymer (*c*) sulphur polymer (*d*) none of these.
4. The S in Buna-S refers to
   (*a*) sodium (*b*) sulphur (*c*) styrene (*d*) just a trade name.
5. The repeating units of PTFE are
   (*a*) $Cl_2CH—CH_3$ (*b*) $F_2C = CF_2$ (*c*) $F_3C—CF_3$ (*d*) $FClC = CF_2$.
6. The inter-particle forces between linear chains in Nylon-66 are
   (*a*) H-bonds (*b*) covalent bonds (*c*) ionic bonds (*d*) unpredictable.
7. Nylon-66 is a polyamide of
   (*a*) vinylchloride and formaldehyde (*b*) adipic acid and methyl amine
   (*c*) adipic acid and hexamethylene diamine (*d*) formaldehyde and malamine.
8. Which of the following is not a condensation polymer ?
   (*a*) Glyptal (*b*) Nylon-66 (*c*) Dacron (*d*) PTFE.
9. Which of the following is a condensation polymer ?
   (*a*) Polystyrene (*b*) Neoprene
   (*c*) PAN (*d*) Poly (ethylene glycol phthalate).
10. The monomer of PVC is
    (*a*) ethylene (*b*) tetra fluoroethylene (*c*) chloroethene (*d*) none of the above.
11. Which of the following polymers is a copolymer ?
    (*a*) Polypropylene (*b*) Nylon-66 (*c*) PVC (*d*) Teflon.
12. Which of the following polymers is a homopolymer ?
    (*a*) Bakelite (*b*) Nylon-66
    (*c*) Terylene (*d*) Neoprene.
13. Which of the following types of polymers has the strongest interparticle forces ?
    (*a*) Elastomers (*b*) Thermoplastics
    (*c*) Fibers (*d*) Thermosetting polymers.
14. Caprolactum is the starting material for
    (*a*) Nylon-6 (*b*) Terylene
    (*c*) Nylon-6, 10 (*d*) Nylon-66.

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15. PDI for natural polymers is generally close to
(a) zero (b) 100 (c) 1 (d) 10.

16. Natural rubber is a polymer of
(a) Butadiene (b) Ethylene (c) Styrene (d) Isoprene.

17. Synthetic polymer prepared by using ethylene glycol and terephthalic acid is known as
(a) Teflon (b) Terylene (c) Nylon (d) PVC.

18. Bakelite is obtained from phenol by reacting with
(a) Ethanal (b) Methanal (c) Vinyl chloride (d) Ethylene glycol.

19. Which of the following is a copolymer ?
(a) Buna-S (b) PVC (c) Orlon (d) Neoprene.

20. Which of the following is a natural fibre ?
(a) Starch (b) Cellulose (b) Rubber (d) Nylon-6.

FILL IN THE BLANKS

1. On the basis of their origin polymers are classified as ..... and ..... polymers.
2. The three natural fibres are .....
3. Natural rubber is a polymer of .....
4. Phenol formaldehyde resin is commonly called .....
5. Nylon-6 is a polymer of .....
6. The monomer units of PAN is .....
7. The monomer units of PMMA is .....
8. In Buna-S, S stands for .....
9. Lucite is a polymer of .....
10. The starting material of PCTFE is .....

TRUE/FALSE STATEMENTS

Which of the following statements are true and which are false ?

1. Neoprene is a synthetic rubber.
2. Cotton is an example of natural polyamide fibre.
3. Buna-S is a homopolymer.
4. Nylon-66 is an example of elastomer.
5. Bakelite is an example of thermosplastic polymer.
6. Polystyrene is an example of thermosplastic polymer.
7. Glyptal is a polymer of phthalic acid and ethylene glycol.
8. Polyethene is a copolymer.
9. Protein is natural polymer.
10. Nylon-6 is a polyamide.

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MATCHING TYPE QUESTIONS

Match the items of column A and B :

Column A	Column B
1. Buna-S	1. Nylon-66
2. Elastomers	2. Wool
3. Addition copolymer	3. Synthetic rubber.
4. Thermosetting polymer	4. Intermolecular forces as hydrogen bonds
5. A polymer of hexamethylene diamine and adipic acid	5. Saran
6. A natural polymer	6. Bakelite

HINTS/ANSWERS

VERY SHORT ANSWER QUESTIONS

1. Natural rubber linear chains
2. Sulphur cross-links are introduced between the chains
3. PTFE (Polytetra fluoroethylene)
4. Bakelite (*thermosetting*) ; polyethene (*thermoplastic*)
5. Nylon-66
6. Polyethylene
7. Terelene
8. Terelene
9. A kind of rubber obtained from the bark of some trees. Here, the carbon chains are trans with respect to C = C bond.
10. Nylon-6.

MULTIPLE CHOICE QUESTIONS

1. (*b*)	2. (*d*)	3. (*b*)	4. (*c*)	5. (*b*)	6. (*a*)
7. (*c*)	8. (*d*)	9. (*d*)	10. (*c*)	11. (*b*)	12. (*d*)
13. (*d*)	14. (*a*)	15. (*c*)	16. (*d*)	17. (*b*)	18. (*b*)
19. (*a*)	20. (*b*)				

FILL IN THE BLANKS

1. Natural, synthetic
2. Wool, Cotton and Silk
3. isoprene
4. bakelite
5. caprolactum
6. acrylonitrile
7. methylmethacrylate
8. sulphur
9. methylmethacrylate
10. chlorotrifluoroethylene

TRUE/FALSE STATEMENTS

1. True	2. False	3. False	4. False	5. False	6. True
7. True	8. False	9. True	10. True		

MATCHING TYPE QUESTIONS

1—3, 2—4, 3—5, 4—6, 5—1, 6—2.

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15

Surfaces and Catalysis

LEARNING OBJECTIVES

In this unit, we shall study the following aspects of surface chemistry :

- *Surfaces : Adsorption*
- *Colloids : Preparation and general properties*
- *Emulsions and micelles*
- *Catalysis : Homogeneous and heterogeneous, Shape selective catalysis.*

There are many properties of matter which are related to their surface. These surface properties become predominant when the material is present in finely divided form or if its surface is rough. Under these conditions, surface area of the material increases enormously and large amount of the substance is present at the surface. In this unit, we shall discuss some of the properties such as *adsorption, colloidal state,* etc. which are directly related to surface effects.

15.1. ADSORPTION

If we consider a liquid or a solid substance then we find that a molecule which is present in the bulk of the substance is being attracted uniformly from all sides by the neighbouring molecules and hence there is no net force acting on the molecule and there are no unbalanced forces of the molecule. On the other hand, if we consider a molecule that is present near the surface, we find that such a molecule is not bonded to other molecules from all sides but has some unutilized valencies because there are no neighbouring molecules above the surface to which it can be bonded. As a result of these unbalanced forces the molecules present at the solid or liquid surfaces tend to satisfy their residual forces by attracting and retaining on their surface, the molecules of other species when brought in contact with them. This results in increase in concentration of the substance near the surface compared with the bulk phases. **A substance which has different concentration at the surface than in the bulk phases is said to *adsorbed* and the existence of a substance at a surface in a different concentration than in the adjoining bulk phases is *adsorption*.**

The material upon whose surface the adsorption takes place is called an **adsorbent** while the molecular species that get adsorbed are called **adsorbate.** The process of removal of an adsorbed substance from the surfaces on which it is adsorbed is called **desorption.** It is reverse of adsorption and can be brought about by heating or by reducing the pressure.

Difference between Adsorption and Absorption

Adsorption is different from absorption. In absorption, the molecules of a substance are uniformly distributed in the bulk of the other, whereas in adsorption molecules of one substance are present in higher concentration at the surface of the other substance. For example, ammonia is absorbed by water whereas it is adsorbed by charcoal. Similarly, water vapours are absorbed by anhydrous calcium

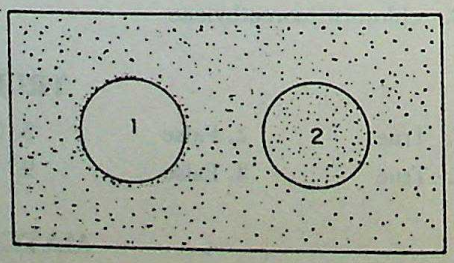

Fig. 15.1. (1) Adsorption, (2) Absorption.

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chloride but are adsorbed by silica gel. The difference between adsorption and absorption is illustrated in Fig. 15.1.

Some important differences between absorption and adsorption are being given below :

Adsorption	*Absorption*
1. It involves unequal distribution of the molecular species in bulk and at the surface.	1. It involves uniform distribution of the molecular species throughout the bulk.
2. It is rapid in the beginning and slown down near the equilibrium.	2. It occurs at a uniform rate.
3. It is a surface phenomenon.	3. It occurs throughout the body of material.

It may be noted that in certain cases absorption and adsorption both take place simultaneously and are non-distinguishable. In such cases the word **sorption** is used to describe the phenomenon.

The forces of adsorption are by virtue of the unbalanced forces or unutilised valencies that are present at the surface. For example, if we take a transition metal then the unbalanced forces in it arises due to the presence of unpaired electrons in the *d*-orbitals.

The forces of adsorption are likely to increase when a solid piece is pulverised to a powder or broken into new surfaces (Fig. 15.2).

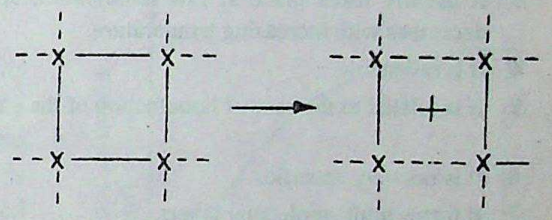

Fig. 15.2. Unbalanced forces at a newly formed surface.

Types of Adsorption

In adsorption, the concentration of one substance is different at the surface of the other substance as compared to adjoining bulk phases. If concentration of adsorbate is more at the surface as compared to its concentration in the bulk phase then this type of adsorption is called **positive adsorption.**

On the other hand, if concentration of adsorbate is less in the surface layer then in the bulk phase then it is called **negative adsorption.** This type of adsorption takes place only in case of solutions.

Depending upon the nature of forces existing between adsorbate molecules and adsorbent, the adsorption can be classified into two types :

(*a*) *Physical adsorption*

(*b*) *Chemical adsorption.*

(*a*) **Physical adsorption.** If the forces of attraction existing between adsorbate and adsorbent are van der Waal's forces, the adsorption is called **physical adsorption.** This type of adsorption is also known as **physisorption** or **van der Waal's adsorption.** Since the forces existing between adsorbent and adsorbate are very weak, therefore, this type of adsorption can be easily reversed by heating or by decreasing the pressure.

(*b*) **Chemical adsorption.** If the forces of attraction existing between adsorbate particles and adsorbent are almost of the same strength as chemical bonds, the adsorption is called **chemical adsorption.** This type of adsorption is also known as **chemisorption or Langmuir adsorption.** Since forces of attraction existing between adsorbent and adsorbate are very strong, therefore, this type of adsorption cannot be easily reversed.

Enthalpy of Adsorption and Free Energy Change

During adsorption, new forces of attraction come into existence. As a result all adsorptions are accompanied by release of energy and are found to be exothermic. ***The enthalpy change taking place for adsorption of one mole of adsorbate on an adsorbent surface is called enthalpy or heat of adsorption.*** In

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general heat of adsorption for chemisorption is more than that of physisorption. Heats of chemisorption are of the order of 200 to 400 kJ mol^{-1} while those of physisorption are generally less than 40 kJ mol^{-1}. A comparison between physical adsorption and chemical adsorption has been given in Table 15.1.

It is also observed that during adsorption there is a decrease in entropy *i.e.* TΔS is negative. Thus, for a process of adsorption,

$$\Delta H = -ve\ ;\ \Delta S = -ve\ ;\ \Delta G = -ve.$$

Table 15.1. Comparison between Physisorption and Chemisorption

Physisorption	*Chemisorption*
1. Low heat of adsorption usually in the range of 20—40 kJ.mol^{-1}.	High heat of adsorption in the range of 40—400 kJ mol^{-1}.
2. Forces of attraction are van der Waal's forces.	Forces of attraction are chemical bond forces.
3. It usually takes place at low temperature and decreases with increasing temperature.	It takes place at high temperature.
4. It is reversible.	It is irreversible.
5. It is related to the ease of liquefaction of the gas.	The extent of adsorption is generally not related to liquefaction of the gas.
6. It is not very specific.	It is highly specific.
7. It forms multi-molecular layers.	It forms monomolecular layers.
8. It does not require any activation energy.	It requires activation energy.

15.2. ADSORPTION OF GASES OF SOLIDS

The extent of adsorption of a gas on a solid adsorbent is affected by the following factors :

(1) *Nature of the gas*
(2) *Nature of the solid*
(3) *Specific area of the solid*
(4) *Pressure of the gas*
(5) *Temperature*
(6) *Activation of adsorbent.*

Let us discuss these factors one by one :

1. Effect of Nature of the Gas

Since physical adsorption is non-specific in nature, every gas will get adsorbed on the surface of any solid to a lesser or greater extent. However, under given conditions of temperature and pressure, the easily liquefiable gases like NH_3, HCl, CO_2, etc., are adsorbed to a greater extent than the permanent gases such as H_2, O_2, N_2, etc. It is because the van der Waal forces or molecular forces are more predominant in the former than in later.

We know that chemisorption is specific in nature. Therefore, in case of chemisorption, a gas gets adsorbed on the solid only if it forms chemical bond with it.

2. Effect of nature of the Adsorbent

Activated charcoal is the most common adsorbent for the gases which are easily liquefied. Most of the poisonous gases such as methane belong to this type and charcoal is commonly used in gas masks. The gases such as H_2, O_2 and N_2 are adsorbed on metals like Ni, Pd, etc.

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3. Specific Area of the Solid

Specific area of an absorbing solid is the surface area available for adsorption per gram of the adsorbent. Greater the specific area of the solid, greater would be its adsorbent power. That is why porous or finely divided forms of adsorbents adsorb strongly. However, the pores should be large enough to allow the gas molecules to enter them.

4. Effect of Pressure of the Gas

In order to understand the effect of pressure on the adsorption of a gas on some solid, we must keep in mind that adsorption is a reversible process and is accompanied by decrease in pressure. Therefore, it is expected that extent of adsorption increases with increase in pressure. The extent of the adsorption is generally expressed as x/m where m is the mass of the adsorbent and x is that of the adsorbate when equilibrium has been attained. ***A graph drawn between extent of adsorption*** $\left(\frac{x}{m}\right)$ ***and the pressure p of the gas at constant temperature is called adsorption isotherm.***

A simple type of adsorption isotherm is shown in Fig. 15.3.

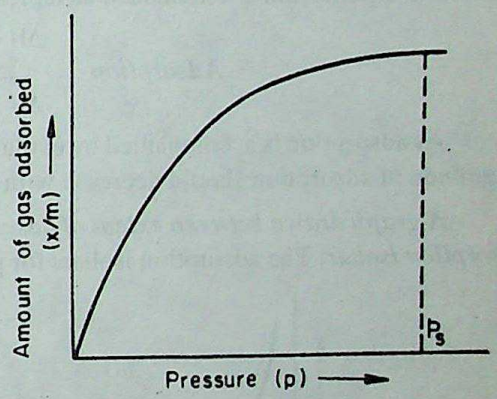

Fig. 15.3. Adsorption isotherm.

At the equilibrium pressure p_s, x/m reaches its maximum value and no more adsorption takes place even if the pressure is further increased. This state is also called saturation state and the corresponding pressure (p_s) is called as *saturation pressure*. Such isotherms are obtained in cases where (*i*) adsorbing gas forms a unimolecular layer on the surface of adsorbent. (*ii*) The adsorbed gas behaves ideally in the vapour phase.

At **low pressures,** the graph is nearly straight and sloping. This indicates that at these pressures x/m is directly proportional to the pressure. This may be put as

$$\frac{x}{m} \propto p^1$$

or

$$\frac{x}{m} = kp^1 \qquad ...(15.1)$$

where k is a constant.

At **high pressures,** *i.e.*, pressure beyond saturation pressure (p_s,) x/m becomes independent of p. In this range of pressures, the relationship between x/m and p may be expressed as

$$\frac{x}{m} \propto p^0$$

or

$$\frac{x}{m} = kp^0 \qquad ...(15.2)$$

At the **intermediate pressures** x/m depends upon p raised to the powers between one and zero. This may be expressed as

$$\frac{x}{m} \propto p^{1/n}$$

or

$$\frac{x}{m} = kp^{1/n} \quad n > 1 \qquad ...(15.3)$$

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Taking logarithms on both sides of Eq. (15.3), we get

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log p \qquad ...(15.4)$$

Thus, if we plot a graph between $\log (x/m)$ and $\log p$, a straight line will be obtained. The slope of the line (Fig.15.4) is equal to $1/n$ and the intercept on $\log (x/m)$ axis will correspond to $\log k$. Therefore, from this graph it is possible to find out value of k and n. The equations (15.3) and (15.4) and the corresponding graphs 15.3 and 15.4 are different expressions of **Freundlich Isotherms.**

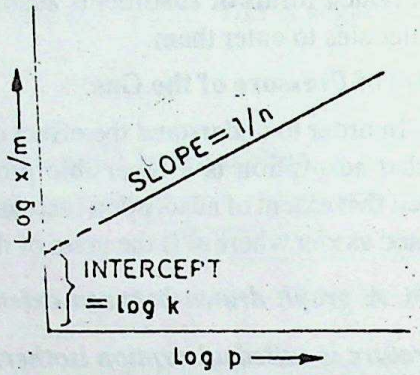


Fig. 15.4. Graph of $\log x/m$ vs. $\log p$.

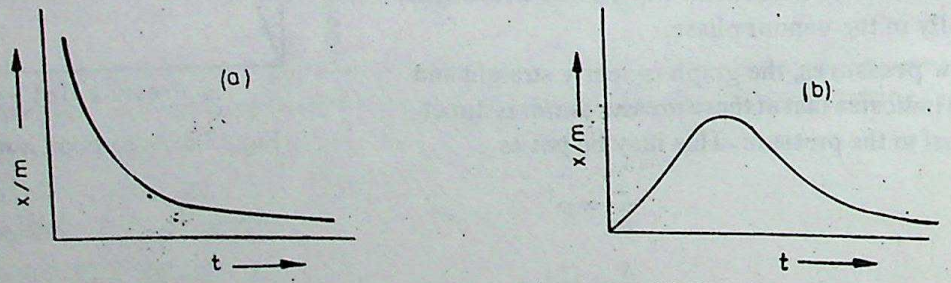
5. Effect of Temperature

As already discussed the adsorption at a surface initially increases till a saturation point is achieved. At this juncture an equilibrium is established as represented below.

$$\textit{Adsorption} \underset{\Delta H = -ve}{\overset{\Delta H = +ve}{\rightleftharpoons}} \textit{Desorption}$$

As adsorption is accompanied by evolution of heat, so in accordance with Le-Chatelier's principle, the magnitude of adsorption should decrease with rise in temperature and this is actually so.

A graph drawn between extent of adsorption (x/m) and temperature (t) at constant pressure is called adsorption isobar. The adsorption isobars for physical adsorption can chemisorption are shown in Fig. 15.5.

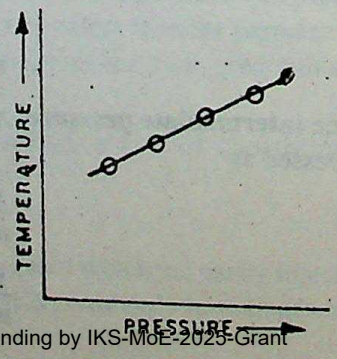


(*a*) Physical adsorption (*b*) Chemisorption

Fig. 15.5. Adsorption isobars.

These isobars are different from each other. While a physical adsorption isobar shows a decrease in x/m as the temperature rises, the isobar of chemisorption shows an increase in the beginning and then a decrease as the temperature rises. This initial increase is due to the fact that, like chemical reactions, chemisorption also requires activation energy.

It is clear from above discussion that as the temperature increases the extent of adsorption decreases. Now in order to get the same amount of adsorption at a higher temperature we need to raise the pressure. Thus, it would mean that a linear relationship would be obtained between temperature and pressure. ***The plot of temperature versus pressure for a given amount of adsorption is called adsorption isostere*** and as shown in figure.



ADSORPTION ISOSTERE

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6. Activation of Adsorbent

Activation of an adsorbent means, increasing the adsorbing power of the adsorbent. This can be achieved in different ways. One possible way of doing it is to increase the specific area of the absorbent. This can be done either by making the surface of adsorbent rough or by breaking it into small pieces. However, if the particles are made very small, then the interparticle spaces will be too small to allow the penetration of gas molecules and hence, the extent of adsorption may decrease.

Adsorbing power of adsorbent can also be increased by certain specific treatments. For example, wood charcoal can be activated by heating it between 650 K and 1330 K in vacuum, air or super-heated steam.

15.3. COMPETING ADSORPTION

There is always a competition between different adsorbates to adsorbs on the adsorbent. ***A strongly adsorbable substance can displace a weakly adsorbed substance.*** For example, on the charcoal taken in gas masks, gases such as O_2, N_2, etc. are already adsorbed. However, in the presence of poisonous gases such as Cl_2 or CH_4, which are very strongly adsorbable, O_2 and N_2 get displaced whereas CH_4 and Cl_2 get adsorbed.

If a mixture of gases is allowed to adsorb on a particular adsorbent, the more strongly adsorbable adsorbate, adsorbs to greater extent than its partial pressure indicates. For example, moisture though present in small proportion in air is strongly adsorbed by silica. Similarly, charcoal also adsorbs polluting gases present in air in small concentrations.

15.4. ADSORPTIONS FROM SOLUTIONS

The process of adsorption can take place even in solutions. It is observed that from the solution containing many solutes certain solutes are adsorbed in more amount as compared with other solutes and solvent. This property is made use of in removing colouring matters from solutions of organic substances. For example, raw sugar solution is decolourized by animal charcoal.

Freundlich adsorption isotherm is found to be applicable even in the adsorption from solutions. However, in place of equilibrium pressures, we use equilibrium concentrations of the adsorbates in the solution.

$$\frac{x}{m} = k\,C^{1/n} \qquad ...(15.5)$$

Taking logarithum, Eq. (15.5) becomes

$$\log \frac{x}{m} = \log k + \frac{1}{n} \log C \qquad ...(15.6)$$

A graph between log x/m and log C is a straight line, similar to graph in Fig. 15.3.

15.5. APPLICATIONS OF ADSORPTION

There are so many applications of adsorption in our life. Some of its applications are given below :

1. Activated charcoal is used **in gas masks** to remove poisonous gases such as CH_4, CO, etc.
2. Animal charcoal is used as **decolorizer** in the manufacture of sugar.
3. Silica is used of removing moisture and **controlling humidity.**
4. A number of industrial processes take place in the presence of **catalysts** which are based upon adsorption.

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5. Adsorption by charcoal cooled in liquid air helps in **creating a high vacuum** in a vessel, which has already been evacuated by a vacuum pump.
6. **Chromatographic purification** of compounds is based upon phenomenon of adsorption.
7. In **volumetric analysis** adsorption indicators such as fluorescein are used.
8. The ion exchange resins used **for removing hardness of water** are also based upon adsorption.
9. The process of adsorption also finds extensive applications in heterogeneous catalysis (*Refer Section 15.18 for details*).

REVIEW QUESTIONS

15.1. Explain why chemisorption has more heat of adsorption than physisorption.

15.2. Give expression for the logarithmic form of Freundlich adsorption isotherm.

15.3. Which is better adsorbent for H_2 gas : charcoal or finely divided palladium ?

15.4. Name three strongly adsorbable gases.

15.5. What do understand by '*specific area*' of an adsorbent ?

15.6. Define the following :

(*i*) Adsorption isobar (*ii*) Adsorption isotherm.

15.7. What is the difference between adsorption isobars for physisorption and for chemisorption ?

15.8. What do you understand by activation of an adsorbent ?

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15.6. COLLOIDAL STATE

Thomas Graham (1861) studied the process of diffusion of dissolved substances through a parchment paper or an animal membrane. He divided substances into two classes :

(*i*) *Crystalloids* and (*ii*) *Colloids.*

Substances like sugar, urea, common salt, etc. which readily passed through the membrane while in the dissolved state were called **crystalloids.** Substances like starch, glue, geltin, etc., which in the dissolved state either do not pass at all or pass through very slowly were called **colloids.**

This arbitrary division of substances into crystalloids and colloids was soon proved to be wrong since a crystalloid could behave as a colloid under different conditions and *vice versa.* For example, common salt, a typical crystalloid in an aqueous solution, behaves as a colloid in the benzene medium while soap, a typical colloid in water behaves as a crystalloid in alcohol. A '*colloidal substance*' therefore, does not represent a separate class of substances. We now speak of the *colloidal state* of matter in which every substance can be obtained by a suitable method. The nature of the substance whether colloid or crystalloid depends upon size of the solute particles. **When the size of solute particles lies between 1 to 100 nm, it behaves as a colloid.** On the other hand, if size of solute particles is greater than 100 nm, it exists as suspension and if particle size is less than 1 nm, it exists as true solution and behave like a crystalloid. Thus, colloid is not a substance but is a particular state of the substance which depends upon size of its particles. The colloidal state is intermediate state between true solution and suspension. A comparison between suspension, colloidal solution and true solution has been given in Table 15.2.

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Table 15.2. Distinction between True Solutions, Colloidal Solutions and Suspensions

Name of Property	*True solutions*	*Colloidal Solutions*	*Suspensions*
1. **Size of particles**	The solute particles in true solutions are molecules having size less than 1 nm.	The particle size in colloidal solution lies in the range of 1 nm to 100 nm.	The size of the particles in the case of suspension is greater than 100 nm.
2. **Visibility of Appearance**	The solute particles are invisible to the naked eye as well as under the most powerful microscope.	The solute particles are invisible to the naked eye but their scattering effect can be viewed with the help of a microscope.	The solute particles are visible even to the naked eye or can be seen with the help of a microscope.
3. **Separation**	The solute and the solvent can not be separated from each other by ordinary filtration or ultrafiltration.	The solute and the solvent cannot be separated from each other by ordinary filtration, but ultra-filtration is possible.	The solute and solvent can be separated by ordinary filtration.
4. **Settling**	The solute particles in the true solution do not settle.	The solute particles in the colloidal solution can be made to settle by centrifugation.	The solute particles in the suspension settle under gravity.
5. **Filtrability**	The solute particles in the true solution diffuse rapidly, pass through a parchment membrane as well as through filter paper.	The solute particles in the colloidal solution do not pass through a parchment membrane, but pass through a filter paper.	The solute particles in the suspension cannot pass the through a parchment membrane or a filter paper.
6. **Tyndall effect**	True solution does not show Tyndall effect.	Colloidal solution shows Tyndall effect.	Suspensions may or may not show Tyndall effects.
7. **Brownian movement**	True solution does not show Brownian movement.	Colloidal solution shows Brownian movement.	Suspension may show Brownian movement.

15.7. PHASES OF COLLOIDAL SOLUTION

It may be noted that colloidal solution is heterogeneous in nature and always consists of at least two phases ; *the disperse phase* and the *dispersion medium*.

(*a*) **Disperse phase.** It is the component present in small proportion and consists of particles of colloidal dimensions (1 – 100 nm).

(*b*) **Dispersion medium.** The medium in which colloidal particles are dispersed is called dispersion medium. In a colloidal solution of sulphur in water, sulphur particles constitutes disperse phase and water constitutes dispersion medium.

The two phases namely ; dispersed and dispersion can be solid, liquid or a gas. Thus, different types of colloidal solutions are possible depending upon the physical state of the two phases. Such types of colloidal solutions are shown in Table 15.3. It is shown be borne in mind that gases between themselves cannot form a colloidal solution due to their property of diffusion to give homogeneous mixtures.

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Table 15.3. Types of Colloidal Solutions

Dispersed phase	*Dispersion medium*	*Common name*	*Example*
Solid	Solid	Solid sol	Coloured gems and glasses, some alloys, rock salt.
Solid	Liquid	Sol	Arsenious sulphide, gold sol, starch, paints, muddy watter.
Solid	Gas	Aerosol	Smoke, duststrom.
Liquid	Solid	Gels	Jellies, cheese, iron hydroxide, shoe polish.
Liquid	Liquid	Emulsion	Milk, cod liver soil.
Liquid	Gas	Liquid aerosol	Mist, fog, cloud, insecticide sprays.
Gas	Solid	Solid foam	Pumicestone, occluded gases, rubber.
Gas	Liquid	Foam	Soap lather, whipped cream, lemonade froth.

The colloidal solutions having fluid-like appearance are called **sols.** The dispersion medium in sols is generally liquid. Colloids are sometimes given specific names depending upon the nature of the dispersion medium. Some common examples are given below :

Dispersion medium	**Name of colloids**
Water	*Hydrosols*
Alcohol	*Alcosols*
Benzene	*Benzosols*
Gases	*Aerosols*

It may be mentioned here that the specific surface area of a substance in colloidal state is very large. For example, let us consider a solid lump of the size one centimetre cube. The surface area of this lump will be 6 cm^2. When the same lump is broken into smaller particles of colloidal dimensions (say 1 nm cube size), the total surface area becomes 6×10^7 cm^2.

15.8. CLASSIFICATION OF COLLOIDS

The classification of colloids on the basis of physical state of disperse phase and dispersion medium has already been discussed in Section 15.7. In this section, we shall discuss their classification on the basis of :

(*i*) *Nature of interaction between disperse phase and dispersion medium*

(*ii*) *Nature of colloidal particles.*

Lyophilic and Lyophobic Sols

Depending upon the interaction between the disperse phase and the dispersion medium, the colloidal sols are classified into two types.

(*a*) *Lyophilic sols*

(*b*) *Lyophobic sols.*

(*a*) **Lyophilic sols.** *In this type of colloidal sols, the disperse phase has great affinity for the dispersion medium.* In such colloids, the dispersed phase does not get easily precipitated and the sols are quite stable. The solids obtained after evaporation may be reconverted to the sol state by simply agitating them with the dispersion medium. Examples of lyophilic sols include sols of gum, gelatine starch, proteins and certain polymers in organic solvents. Such sols are called **reversible sols.** If water is the dispersion medium, these are called *hydrophilic sols.*

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(*b*) **Lyophobic sols.** *In this type of sols, disperse phase has little affinity for the dispersion medium.* These sols are relatively less stable than lyophilic sols. These sols are easily precipitated (or coagulated) on the addition of small amounts of electrolytes, by heating or by shaking. These are *irreversible* as their precipitated mass cannot be brought back into the colloidal state by simply shaking them up with the dispersion media. Examples of lyophobic sols include sols of metals, and their insoluble compounds like sulphides and oxides. They need stabilizing substances for preservation. If water is the dispersion medium, these are known as *hydrophobic sols*.

The distinction between lyophilic and lyophobic sols is given in Table 15.4.

Table 15.4. Distinction between Lyophilic and Lyophobic Sols

Lyophobic sols	*Lyophilic sols*
1. They are irreversible sols.	The are reversible sols.
2. They are less stable and get coagulated by electrolytes, by heating or by agitating.	The are quite stable are not easily coagulated by electrolysis.
3. They are prepared by indirect methods which are not so easy.	They are obtained by simple solution method, *e.g.*, starch solution.
4. The are obtained from inorganic materials such as metals, metal sulphides, metal hydroxides, etc.	The are obtained from organic materials such as starch, gum, gelatin, etc.
5. These are unstable and hence require stablizers.	These are self-stablized.
6. The particles are not hydrated.	The particles are hydrated.

Multimolecular, Macromolecular and Associated Colloids

Depending upon nature of the particles, the colloidal solutions are classified as :

(*a*) *Multimolecular colloids,*

(*b*) *Macromolecular colloids and*

(*c*) *Associated colloids.*

(*a*) **Multimolecular colloids.** *In this type of colloids, colloidal particles are aggregates of atoms or small molecules with molecular size less than 1 nm.* For example, a gold sol consists of particles of various sizes which are clusters of several gold atoms. A sol of sulphur consists of colloidal particles which are aggregates of S_8 molecules. These molecules in the aggregate are held by van der Waal's forces.

(*b*) **Macromolecular colloids.** *In this type of colloids, colloidal particles are themselves large molecules having colloidal dimensions.* They have very high molecular masses varying from thousands to millions. Naturally occurring macromolecules are such as starch, proteins and cellulose. Artificial macromolecules consist of polymers such as polyethylene, nylon, plastics, polystyrene, etc. These colloidal solutions resemble true solutions in some respects.

(*c*) **Associated colloids.** There are certain substances which behave as normal, strong electrolytes at low concentration but at higher concentration they behave as colloidal solutions due to the formation of aggregated particles. Such colloids are called associated colloids and the aggregated particles are called **micelles.** Soaps and detergents are example of associated colloids.

For detailed discussion about micelles refer to Section 15.16.

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15.9. PREPARATION OF COLLOIDAL SOLUTIONS

For the preparation lyophobic and lyophilic sols different types of methods are employed :

Preparation of Lyophobic Sols.

Lyophobic sols can be prepared by two types of methods :

1. *Condensation methods* ; and
2. *Dispersion methods*.

1. Condensation Methods

In this type of methods particles of atomic or molecular size are induced to combine to form aggregates having colloidal dimensions. For this purpose chemical as well as physical methods can be applied.

(*i*) **By chemical methods.** Colloidal solutions can be prepared by chemical reactions involving, double decomposition, oxidation, reduction and hydrolysis.

(*a*) *Double decomposition.* A colloidal sol of arsenious sulphide is obtained by passing hydrogen sulphide into a solution of arsenious oxide in distilled water.

$$As_2O_3 + 3H_2S \longrightarrow As_2S_3 + 3H_2O$$

Sols of silver halides are obtained by mixing dilute solutions of silver salts and alkali halides in equivalent amounts. Silica gel sol is prepared by this method between dilute solutions of sodium silicate and HCl.

(*b*) *Oxidation.* A colloidal solution of sulphur can be obtained by passing hydrogen sulphide into a solution of sulphur dioxide in water or through a solution of an oxidizing agent (bromine water, nitric acid, etc.).

$$SO_2 + 2H_2S \longrightarrow 3S + 2H_2O$$

$$H_2S + [O] \longrightarrow H_2O + S$$

(*c*) *Reduction.* A colloidal solution of a metal like silver, gold and platinum can be prepared by reducing its salt solution with a suitable reducing agent, such as stannous chloride, formaldehyde, hydrazine, etc.

$$2AuCl_3 + 3SnCl_2 \longrightarrow \underset{\text{Gold sol}}{2Au} + 3SnCl_4$$

(*d*) *Hydrolysis.* This method is used to prepare hydroxides and oxides of weakly electro-positive metals like Fe, Al or Sn. A red sol of ferric hydroxide is obtained by the hydrolysis of ferric chloride with boiling water.

$$FeCl_3 + 3H_2O \rightleftharpoons Fe(OH)_3 + 3HCl$$

(*ii*) **By physical methods.** (*a*) *By exchange of solvent.* When a true solution is mixed with an excess of the other solvent in which the solute is insoluble but solvent is soluble, a colloidal solution is obtained. For example, when a solution of sulphur in alcohol is poured in excess of water, a colloidal solution of sulphur is obtained.

(*b*) *By excessive cooling.* The colloidal solution of ice in an organic solvent such as $CHCl_3$ or ether can be obtained by freezing a solution of water in the solvent. The molecules of water which can no longer be held in solution separately combine to form particles of colloidal size.

2. Dispersion Methods

In these methods large particles of the substance are broken into particles of colloidal dimensions in the presence of dispersion medium. Since the sols formed are highly unstable. They are stabilized by adding some suitable stabilizer. Some of the methods employed for carrying out dispersion are given as follows :

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(*a*) *Mechanical dispersion.* In this method, the coarse suspension of the substance is brought into a colloidal state in the dispersion medium by grinding it in a colloid mill (Fig. 15.6), ball mill or ultrasonic disintegrator. The colloid mill consists of two metal discs, close together, rotating at high speed (7,000 revolutions per minute) in opposite direction when the suspension particles are torn off to the colloidal size.

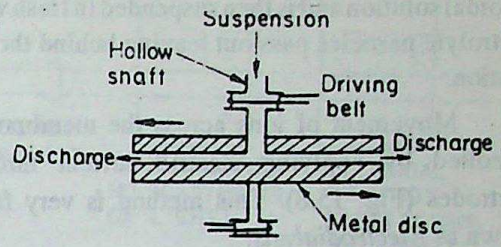

Fig. 15.6. A colloid mill.

(*b*) *Electrical disintegration or Bredig's arc method.* This process involves dispersion as well as condensation. Colloidal solutions of metals such as gold, silver, platinum, etc., can be prepared by this method. In this method, electric arc is struck between electrodes of the metal immersed in the dispersion medium (Fig. 15.7). The intense heat produced vaporizes some of the metal, which then condenses to form particles of colloidal size.

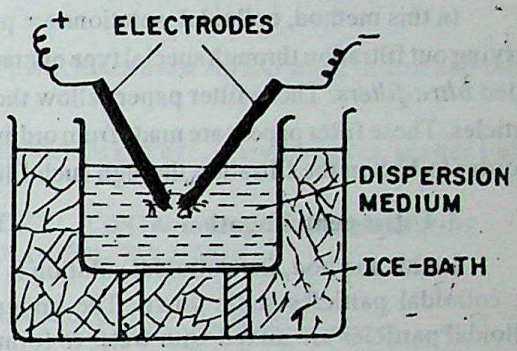

Fig. 15.7. Bredig's method.

(*c*) *Peptization.* Peptization may be defined *as the process of converting a precipitate into colloidal form by shaking it with dispersion medium in the presence of small amount of electrolyte.* The electrolyte used for this purpose is called peptizing agent. This method is applied, generally, to convert fresh precipitate into colloidal solution because such precipitates are simply clusters of particles of colloidal size held by weak forces.

Cause of peptization. *During peptization, the precipitate adsorbs one of the ion of the electrolyte on its surface. The adsorbed ion is generally common with those of the precipitate. This causes the development of positive or negative charge on precipitates* which ultimately break up *into smaller particles having the dimensions of colloids.* For example, when freshly precipitated $Fe(OH)_3$ is shaken with aqueous solution of $FeCl_3$ (peptizing agent) it adsorbs Fe^{3+} ions and thereby break up into small-sized particles of the type $[Fe(OH)_3]Fe^{3+}$. Similarly, a precipitate of AgCl on shaking with dilute solution of $AgNO_3$ adsorbs Ag^+ ion and get peptized to colloidal particles of the type $[AgCl]Ag^+$. In some cases, peptization can also be achieved by organic solvents. For example, cellulose nitrate is peptized by ethanol. The colloidal solution so obtained is known as *collodion.*

Preparation of Lyophilic Sols

Lyophilic sols are quite stable and can be easily prepared by shaking the material to be dispersed with dispersion medium. Some examples are : colloidal solutions of gelatin, gum, starch, egg albumin, etc.

15.10. PURIFICATION OF COLLOIDAL SOLUTIONS

The colloidal solutions obtained by various methods are impure and contain impurities of electrolytes and other soluble substances. These impurities may destabilize the sol. Hence, they have to be removed. A very important method of removal of soluble impurities from sols by semi-permeable membrane is known as *Dialysis.*

1. Dialysis

Particles of true solutions can pass through parchment paper or cellophane membrane. On the other hand, sol particles cannot pass through these membranes. A bag made up of such a members is filled with the

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colloidal solution and is then suspended in fresh water. The electrolyte particles pass out leaving behind the colloidal solution.

Movement of ions across the membrane can be expedited by applying electric current through two electrodes (Fig. 15.8). This method is very fast and is known as *Electrodialysis*.

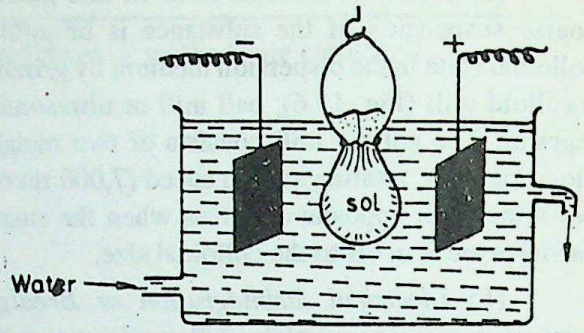

Fig. 15.8. Electrodialysis.

2. Ultra-filtration

In this method, colloidal solutions are purified by carrying out filtration through special type of graded filters called *ultra-filters*. These filter papers allow the electrolytes to pass through them but do not allow colloidal particles. These filter papers are made from ordinary filter papers by impregnating them with colloidal particles. In order to hasten the filtration through such filter papers increased pressure or suction is required.

3. Ultra-centrifugation

In this method, the colloidal solution is placed in a high speed centrifugal machine. On centrifuging, the colloidal particles settle down. The impurities remain the centrifugate and are removed. The settled colloidal particles are mixed with water to form the colloidal solution again.

REVIEW QUESTIONS

15.9. Out of lyophilic and lyophobic sols, which sol is more stable ?

15.10. Out of the following which is an example of lyophilic sol ?

(*i*) Gold sol (*ii*) Phosphorus sol (*iii*) Starch sol.

15.11. Give an example of macromolecular colloid.

15.12. How would you prepare a colloidal solution of sulphur by chemical methods ?

15.13. Suggest a physical method for the preparation of phosphorus sol.

Hint. Solvent exchange method.

15.14. Given two main differences between lyophilic and lyophobic colloids.

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15.11. PROPERTIES OF COLLOIDAL SOLUTIONS

1. Heterogeneous nature. Colloidal system is of two phases : (*a*) *dispersed phase* and (*b*) *dispersion medium*. In a colloidal solution, each particle is contained within its own boundary surfaces which separate it from the dispersion medium.

2. Colligative properties—*osmotic pressure*. Due to high average molecule masses of colloidal particles, they give very low mole fractions in colloidal solution. Hence, they possess low osmotic pressure. Due to the same reason, in colloidal solutions, elevation in boiling point and depression in freezing point is also very small.

3. Filtrability. The size of the colloidal particles is less than the pores of the filter paper, and therefore, they easily pass through a filter paper. Colloidal particles, however, cannot pass through the parchment paper or an animal membrane or ultrafilter.

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4. Optical properties. *Tyndall Effect.* Tyndall, in 1869, observed that if a strong beam of light is passed through a colloidal solution placed in dark place, the path of the beam gets illuminated by a bluish light (Fig. 15.9). This phenomenon is called **Tyndall effect.** The phenomenon is due to the scattering of light by the colloidal particles.

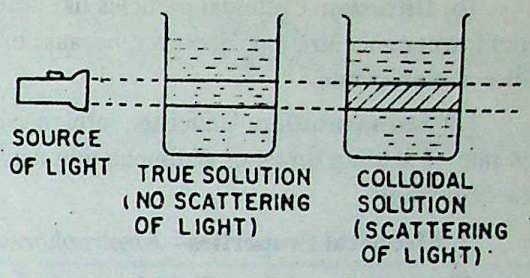

Fig. 15..9. Tyndall effect.

The same phenomenon is noticed due to scattering of light by dust particles, when a beam of sunlight enters a dark room through a slit.

True solutions do not exhibit Tyndall effect because the particles in them are too small in size and they do not cause any scattering.

5. Visibility. Colloidal particles are tool small to be seen with naked eye. They however, scatter light and becomes visible as **bright spots** or **discs of light** against a black background when viewed through an **ultramicroscope.** Zsigmondy (1903) devised this microscope based on the principle of scattering of light by colloidal particles. The arrangement of the instrument is shown in Fig. 15.10. A strong beam of light is focused by a series of lens-combinations in a vessel containing the sol. The colloidal solution is seen through a microscope placed at right angle to the beam.

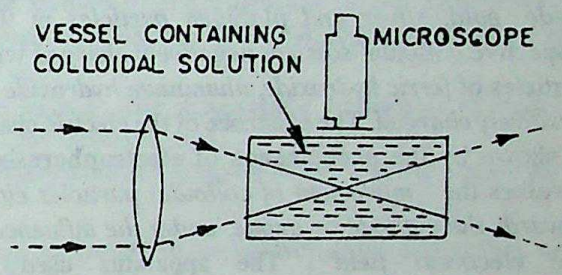

Fig. 15.10. Ultra-microscope.

6. Mechanical Properties

(*a*) **Brownian movement.** Robert Brown, a botanist discovered in 1827 that **pollen grains** placed in water do not remain at rest but move about continuously and randomly. Later on, this phenomenon was observed in case of colloidal particles when they were seen under the ultramicroscope. The particles were seen to be in constant motion in zig-zag path in all possible direction (Fig. 15.11). *This zig-zag motion of colloidal particles is called* **Brownian movement.**

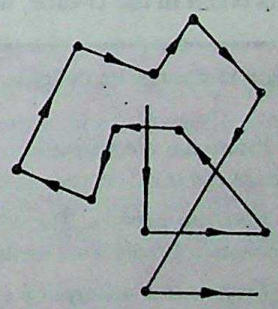

Fig. 15.11. Brownian movement.

Cause of Brownian movement. *Brownian movement arises because of the impacts of the molecules of the dispersion medium with the colloidal particles. It has been postulated that the impacts of the particles of the dispersion medium on the colloidal particle are unequal which ultimately causes its zig-zag motion. However, as the size of the particle increases, the probability of unequal impacts decreases and the Brownian movement becomes slow. Ultimately, when the dispersed particle becomes bigger enough to acquire the dimensions of suspension, no Brownian movement is observed.*

Significance of Brownian movement

(*i*) Brownian movement provides a direct demonstration of ceaseless motion of molecules as postulated by kinetic theory.

(*ii*) It counters the force of gravity acting on colloidal particles and hence helps in providing stability to colloidal sols.

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(*b*) **Diffusion.** Colloidal particles like solute particles diffuse from a region of higher concentration to that of lower concentration. However, because of their bigger sizes colloidal particles move slowly and hence diffuse at slower rate.

(*c*) **Sedimentation.** Under the influence of gravity, the sol particles tend to settle down very slowly. This rate of settling down or sedimentation can be accelerated by the use of a high speed centrifuge called *ultra-centrifuge.*

7. Electrical Properties—*Electrophoresis*

The particles of the colloidal solution are electrically charged and carry same type of charge ; either positive or negative. The dispersion medium has an equal and opposite charge making the system neutral as a whole. Due to similar nature of the charge carried by the particles, they repel each other and do not combine to form bigger particles. That is why, a sol is stable and particles do not settle down. *Arsenious sulphide, gold, sliver and platinum particles* in their respective colloidal sols are *negatively charged* while particles of *ferric hydroxide, aluminium hydroxide* are *positively charged.* The existence of the electric charge is shown by the phenomenon of **electrophoresis.** It involves the "*movement of colloidal particles either towards the cathode or anode, under the influence of the electrical field*". The apparatus used for electrophoresis is shown in Fig. 15.12.

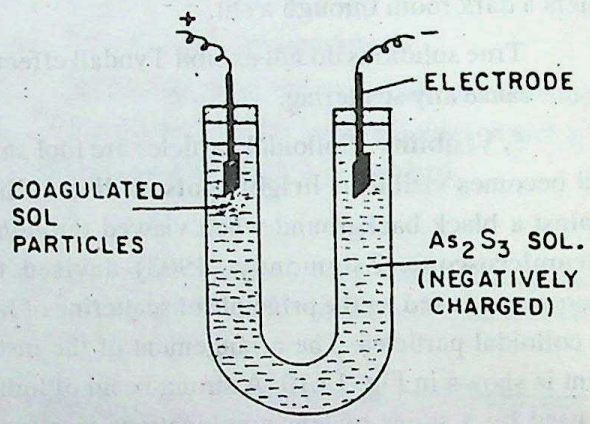

Fig. 15.12. Electrophoresis.

The colloidal solution is placed in a U-tube fitted with platinum electrodes. On passing an electric current, the charged colloidal particles move towards the oppositely charged electrode. Thus, if arsenious sulphide sol is taken in the U-tube, its particles move towards the anode.

Origin of charge on colloids. The reasons for the origin of electrical charge on colloidal particles are given below :

(*i*) ***Frictional electrification.*** The rubbing of colloidal particles with molecules of dispersion medium leads to appearance of electrical charges on colloidal particles.

(*ii*) ***Electron capture.*** The colloidal particles may acquire charge by capturing electrons from air or during electro-dispersion in Bredig's are method.

(*iii*) ***Preferential adsorption of ions from solutions.*** An ionic colloid adsorbs ions common to its own lattice structure. Thus, AgCl particles can adsorb Cl^- ions if excess of KCl solution is used for its preparation whereas, if it is prepared by using excess of $AgNO_3$ solution it adsorbs Ag^+ ions from solutions. The sol will be negatively charged if it adsorbs Cl^- ions and positively charged if it adsorbs Ag^+ ions.

Similarly, if $Fe(OH)_3$ sol is prepared by hydrolysis of $FeCl_3$ by hot water, there is adsorption of Fe^{3+} ions and particles acquire positive charge. On the other hand, if the sol is prepared by adding excess of NaOH solution to $FeCl_3$ solution, then, there is adsorption of OH^- ions and the colloidal particles acquire negative charge.

(*iv*) ***Dissociation of surface molecules.*** Soaps expel alkali ions to acquire a negative charge. Dye particles can dissociate to furnish positive or negative ions in the solution according to their composition.

(*v*) ***Dissociation of molecular electrolytes adsorbed on the surface of particles.*** H_2S molecules get adsorbed on sulphides during precipitation. By dissociation of H_2S, hydrogen ions are lost and the colloidal particles become negatively charged due to sulphide (S^{2-}) ions which are left on the colloidal particles.

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Some common positively charged and negatively charged colloids are given below :

Positively charged : $Fe(OH)_3$ sol, $Cr(OH)_3$ sol, $Al(OH)_3$ sol, $Ca(OH)_2$ sol, TiO_2, dyes like methylene blue and haemoglobin.

Negatively charged : As_2S_3, Sb_2S_3, CdS, metal sols like Cu, Au, Pt, Ag, etc. ; and acid dyes, like congo red.

15.12. COAGULATION OF COLLOIDAL SOLUTIONS

Presence of small concentrations of appropriate electrolytes is necessary to stabilize the colloidal solutions. However, if the electrolytes are present in higher concentration, then the ions of the electrolyte neutralize the charge on the colloidal particles. Now these colloidal particles may unite together to form bigger particles which are then precipitated. ***The precipitation of a colloid through induced aggregation by the addition of some suitable electrolyte is called coagulation of flocculation.***

The coagulation of a colloidal solution by an electrolyte does not take place until the added electrolyte has certain minimum concentration in the solution. ***The minimum concentration of the electrolyte in millimoles per litre of the mixed solution, required to cause coagulation of a particular sol is called the coagulation or precipition value of the electrolyte for the sol.***

Different electrolytes have different coagulation values. The coagulation behaviour of various electrolytes was studied in details by Hardy and Schulze. They observed that :

(*i*) *The ions carrying charge opposite to that of sol particles are effective in causing the coagulation of the sol.*

(*ii*) *Coagulating power of an electrolyte is directly proportional to the valency of the active ions, i.e., ions causing coagulation.*

Thus, for the coagulation of sols carrying negative charge (like As_2S_3 sol), Al^{3+} ions are more effective than Ba^{2+} or Na^+ ions. Similarly, for the coagulation of sols carrying positive charge, such as $Fe(OH)_3$ sol PO_4^{3-} ions are more effective than SO_4^{2-} or Cl^- ions. The two observations given above are collectively called **Hardy Schulze rule.**

Coagulation of colloidal solutions can also be achieved by the following methods :

(*i*) **By mutual precipitation.** When two oppositely charged sols (such as $Fe(OH)_3$ and As_2S_3) are mixed in equi-molar proportions, they neutralise each other and may get coagulated. Sometimes the sols may get coagulated due to the mutual destruction of stabilizing agents.

(*ii*) **By electrophoresis.** We know that during electrophoresis the sol particles move towards the oppositely charged electrodes. If the process is carried for a long time, the particles will touch the electrode, lose their charge and get coagulated.

(*iii*) **By repeated dialysis.** The stability of colloidal sols is due to the presence of a small amount of electrolyte. If the electrolyte is completely removed by repeated dialysis, the sol will get coagulated.

(*iv*) **By heating.** The sol may be coagulated even by simple heating.

15.13. INTERACTION BETWEEN COLLOIDS—GOLD NUMBER

As already discussed, lyophobic sols are highly unstable and are generally stabilized by adding stabilizers. When two lyophobic sols are mixed together, it may result in coagulation because of mutual neutralization of electrical charges or due to destruction of each other's stabilizers. However, when a lyophilic sol is mixed with lyophobic sol, it is observed that in many cases *lyophilic sols exert protecting influence on lyophobic sols against their coagulation by electrolytes.* This is presumably because the lyophilic particles form a protective layer around the lyophobic particles. For example, a gold sol or a silver sol, protected by gelatin, gum or starch may not be coagulated easily. Different lyophilic sols exert protective influence to different extent. The protecting power of a protective colloid is expressed in terms of **gold number** which may be defined as :

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The number of milligrams of the protective colloid which just prevent coagulation of 10 ml of standard gold sol when 1 ml of 10% solution of sodium chloride is added to it.

The coagulation is detected by the change of colour of the gold sol from red to blue. It may be noted that *smaller the gold number of the protective colloid is,* greater will be its *protective power*. The gold number of a few protective colloids are given below :

Gum-arabic	:	0.15 – 0.25	*Haemolgobin*	:	0.03
Gelatin	:	0.005 – 0.01	*Caseinate*	:	0.01
Egg albumin	:	0.15 – 0.25	*Sodium oleate*	:	0.4
Potato starch	:	25	*Dextrin*	:	6 – 20

15.14. GELS

Certain sols have the property of setting to a semi-solid, jelly—like form by enclosing the entire amount of liquid within itself when they are present at high concentrations. This process in called *gelation* and *colloidal systems with jelly-like appearance* are known as **gels.** Some common examples of gels are : *gum arabic, gelatin, agar, processed cheese, silicic acid, ferric hydroxide,* etc.

Gels possess rigid structures which are formed when the *particles of dispersed phase* get interlocked and create a loose network frame. The particles of dispersion medium are trapped within the loose framework. The degree of rigidity of structure varies from substance to substance. Thus, gel represents a liquid-solid system *i.e.*, a liquid dispersed in a solid.

When the gels are allowed to stand for long time, they give out small quantity of trapped liquid which accumulates on its surface. This action of gels is known as **syneresis** or **weeping.**

Gels are divided into two categories *i.e.*, **elastic gels** and **non-elastic gels.** The characteristic differences between the two are tabulated below :

Elastic gels	*Non-elastic gels*
1. These gels change to solid mass on dehydration which can be changed back to original form by addition of water followed by warming.	1. These gels change to solid mass on dehydration which cannot be changed back to original form by addition of water and warming.
2. They absorb water when placed in it with simultaneous swelling of gel body. This phenomenon is called **imbibition.**	2. These do not imbibe.

Some gels such as silica, gelatin, ferric phosphate, etc., liquify on mechanical shaking and change to sols losing their semi-solid gel character. The sol on standing changes back to the gel. This phenomenon is called **thixotropy.**

15.15. APPLICATIONS OF COLLOIDS

Due to the presence of electrical charge on colloidal particles, colloidal solutions are somewhat good conductors. This fact finds many important applications, some of which are given below :

1. Rubber plating. The negatively charged rubber particles from the rubber sol are deposited on wares, handles of different tools, rubber gloves, etc., by electroplating.

2. Sewage disposal. Sewage water contains particles of dirt, rubbish, etc., which are of colloidal size, carry charge and, therefore do not settle down easily. These particles can be removed by electrophoresis. Dirty

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water is passed through a tunnel fitted with metallic electrode which is maintained at high potential difference. The particles migrate to the oppositely charged electrode, lose their charge and are coagulated. The deposited matter is used as a manure and the water left behind is used for irrigation.

3. Cottrell smoke precipitator. Smoke is made free of colloidal particles by passing it through cottrell precipitator installed in the chimney of an industrial plant. It consists of two metal discs charged to a high potential. The charge on the colloidal dust and carbon particles of smoke is neutralised and they are precipitated down, while free gases come out through the chimney.

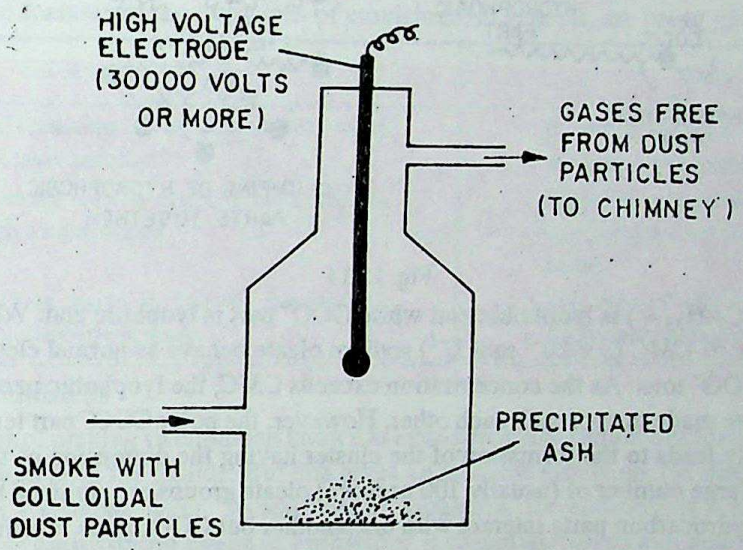

Fig. 15.13. Cottrell smoke precipitator.

4. Formation of delta. River water is a sort of colloidal solution of clay in water. Sea water, on other hand, contains a large number of dissolved salts and is a sort of electrolyte. When river water comes in contact with sea water coagulation of colloidal particles occurs. These coagulated clay particles settle down at the point of contact and gradually river bed starts rising. This leads river water to adopt different course and ultimately results in the formation of *delta*.

5. Artificial rain. Artificial rain is caused by spraying oppositely charged colloidal dust or sand particles over the clouds by aeroplane. The colloidal water particles of the clouds get neutralised and coagulate to bigger water drops which cause artificial rain.

6. Purification of water. The colloidal particles present in water can be precipitated by addition of small amount of alum ($K_2SO_4.Al_2(SO_4)_3.24H_2O$). The Al^{3+} ions furnished by alum help in coagulation of impurities which are present in the colloidal form.

15.16. MICELLES

It has been pointed out earlier that certain substances like soaps and detergents behave as electrolytes at low concentration. However, at high concentrations they constitute colloidal sols, which are known as *associated colloids*. The colloidal behaviour of such substances is due to the formation of aggregates or clusters in solutions. Such aggregated particles are known as *micelles*. Thus, **micelle** may be defined as *the cluster or aggregated particles formed by association colloids in solutions*. The formation of micelle takes place above certain concentration called ***critical micellization concentration*** (CMC). Every micelle system has a specific value of CMC.

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Mechanism of Micelle Formation

Micelles are generally formed by the specific type of molecules which have *lyophilic* as well as *lyophobic ends*. Such molecules are known as *surface active molecules* or *surfactant molecules*. Sodium oleate, $C_{17}H_{33}COO^- Na^+$ (one of the soaps) is a typical example of such type of molecules. The long hydrocarbon

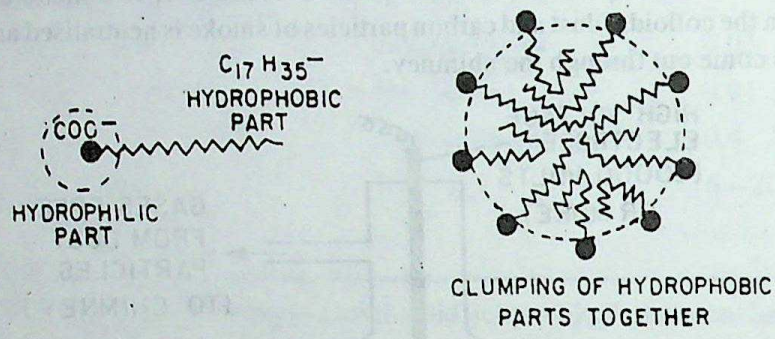

Fig. 15.14

part of oleate radical ($C_{17}H_{33}-$) is lyophobic end while COO^- part is lyophilic end. When the concentration of the solution is below its *CMC* (3×10^{-3} mol L^{-1}) sodium oleate behave as normal electrolyte and ionises to give Na^+ and $C_{17}H_{33}COO^-$ ions. As the concentration exceeds *CMC*, the lyophobic part starts receding away from the solvent and are made to approach each other. However, the polar COO^- part tend to interact with the solvent. This ultimately leads to the formation of the cluster having the dimension of the colloidal particles. In each such cluster a large number of (usually 100 or more) oleate groups are clumped together in a spherical manner so that their hydrocarbon parts interact with one another but COO^- parts remain projected in water.

Some other examples of micelle systems are :

(*i*) Sodium lauryl sulphate ; $CH_3(CH_2)_{11}SO_4^- Na^+$

(*ii*) Sodium stearate ; $CH_3(CH_2)_{16} COO^- Na^+$

(*iii*) Cetyl trimethyl ammonium bromide ; $CH_3(CH_2)_{15}(CH_3)_3N^+Br^-$.

15.17. EMULSIONS

Emulsions are colloidal solutions in which disperse phase as well as dispersion medium are liquids. Emulsions can be broadly classified into two types :

(*i*) *Oil in water emulsions.* In this type of emulsions, oil acts as disperse phase and water acts as dispersion medium. Some examples of this type of emulsions are milk, vanishing cream, etc.

(*ii*) *Water in oil emulsions.* In this type of emulsions, water acts as disperse phase and oil acts as dispersion medium. For example, cold cream, butter, cod liver oil, etc.

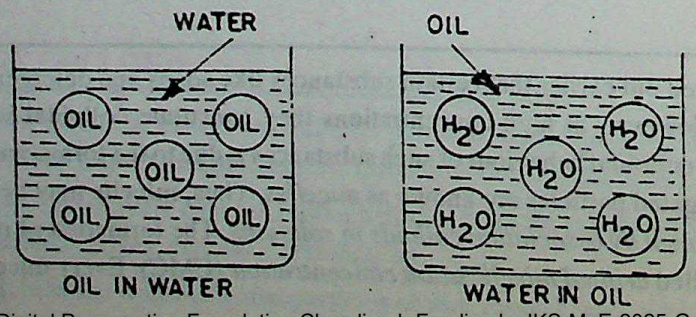

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Fig. 15.15

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Identification of Emulsions

The following tests may be employed to distinguish between the two types of emulsions :

(*i*) *Dye test.* To the emulsion some oil soluble dye is added. If the background becomes coloured, the emulsion is water-in-oil type and if the droplets become coloured, the emulsion is oil-in-water type.

(*ii*) *Dilution test.* If the emulsion can be diluted with water, this indicates that water is the dispersion medium and the emulsion is of oil-in-water type. In case the added water forms a separate layer, the emulsion is water-in-oil type.

Distinctive features of the two types of emulsions, in general, are being given in tabular form.

Oil in water type	*Water in oil type*
1. This type of emulsion can be diluted with water. No separate layer results.	It cannot, be diluted with water. On dilution, a separate layer forms.
2. On adding an oil soluble dye, coloured droplets are seen with a microscope.	When an oil soluble dye is added to the emulsion, on coloured droplets are seen with a microscope.
3. This type of emulsion is less viscous and its electrical conductivity is more.	This type of emulsion is more viscous and its electrical conductivity is less.

Preparation of Emulsions

The process of making an emulsion known as *emulsification.* Emulsions may be obtained by vigorously agitating a mixture of both the liquids. But this gives an unstable emulsion, the dispersed drops at once come together and form a separate layer. To stabilize an emulsion, the addition of a small quantity of the third substance known as **emulsifying agent** or **emulsifier** is essential. Soaps and detergents are most frequently used as emulsifiers. They coat the drops of an emulsion and check them from coming together and the emulsion is, thus, stabilized. The other common stabilizing agents are proteins, gum and agar.

Demulsification. *The decomposition of an emulsion into its constituent liquids is called demulsification.* The various techniques applied for demulsification are *freezing, boiling, filtration, centrifugation, electrostatic precipitation or chemical methods* which destroy the *emulsifying agents.* For example, cream is separated from milk by centrifugation.

Application of Emulsions. Some important applications of emulsions are being discussed as follows :

1. Cleansing action of soap. Washing action of soap is due to the emulsification of grease and taking it away in the water along with dirt or dust present on grease.

Explanation. The cleansing action of soap can be explained keeping in mind that a soap molecule contains a non-polar hydrophobic group and a polar hydrophilic group. The dirt is held on the surface of clothes by the oil or grease which is present there. Since oil or grease are not soluble in water, therefore, the dirt particles cannot be removed by simply washing the cloth with water. When soap is applied, the non-polar alkyl group dissolves in oil droplets while the polar —COO^-Na^+ groups remain dissolved in water (Fig. 15.16). In this way, each oil droplet is surrounded by negative charge. These negatively charged oil droplets cannot coalesce and a stable emulsion is formed. These oil droplets (containing dirt particles) can be washed away with water along with dirt particles.

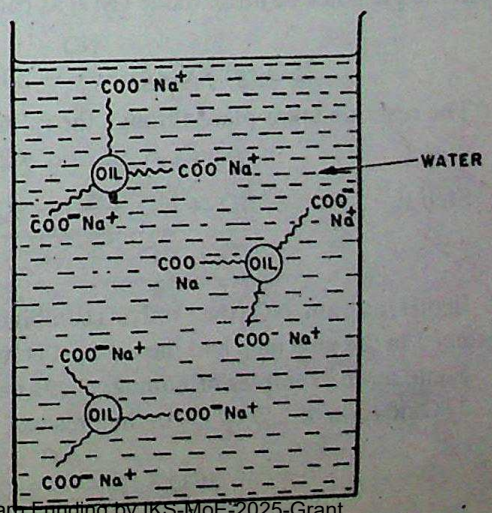

Fig. 15.16. Cleansing action of soaps.

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2. In medicines. A wide variety of pharmaceutical preparations are emulsions. For example, emulsion of cod liver oil. These emulsified oils are easily acted upon by the digestive juices in the stomach and, hence, are readily digested.

3. Digestion of fats. Digestion of fats in the intestines is aided by emulsification. A little of the fat forms a sodium soap with the alkaline solution in the intestine, and this soap emulsifies the rest of the fat. It is easier for the digestive enzymes to carry out their functions on emulsified fat.

4. In disinfectants. The disinfectants such as dettol and lysol give emulsions of the oil-in-water type when mixed with water.

5. In metallurgical operations. Emulsions play an important role in industry. The metal ores are concentrated by froth-flotation process which involves the treatment of the pulverized ore in emulsion of pine oil.

REVIEW QUESTIONS

15.15. Give an example of positively charged sol.

15.16. What is the charge on sol particles in arsenious sulphide sol ?

15.17. Out of sodium chloride and barium chloride which will have greater coagulation value for As_2S_3 sol ?

15.18. Out of sodium chloride and sodium sulphate which will have greater coagulating power for $Fe(OH)_3$ sol ?

15.19. Gold numbers of gelatin and gum arabic are .005 and 0.15 respectively, which of two has greater protecting power ?

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15.18. CATALYSIS

We have already studied that a catalyst is a substance which increases the rate of a chemical reaction without itself being used up in the reaction. According to modern view, a catalyst speeds up the reaction by providing an alternate path of lower activation energy. The catalyst lowers the activation energy by interacting with reactants leading to the formation of some intermediate. In due course, the intermediate compound is consumed and the catalyst is regenerated.

When a catalyst mixes homogeneously with the reactants and forms a single phase, the catalyst is said to be **homogeneous** and this type of catalysis is called **homogeneous catalysis.** For example, SO_2 is oxidized to SO_3 in the presence of nitric oxide (NO) as catalyst.

$$2SO_2(g) + O_2(g) \xrightarrow{NO} 2SO_3(g)$$

The reaction takes place through the following mechanism :

Step I $\quad 2NO + O_2 \longrightarrow 2NO_2$

Step II $\quad SO_2 + NO_2 \longrightarrow SO_3 + NO] \times 2$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

In this reaction, NO (the catalyst) combines with oxygen to form NO_2 (intermediate). The intermediate is consumed in the next step and the catalyst is regenerated.

Some more examples of homogeneous catalysis are :

1. Oxidation of CO by O_2 in the presence of NO as catalyst.

$$2CO + O_2 \xrightarrow{NO} 2CO_2$$

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2. Preparation of diethyl ether from ethyl alcohol using conc. H_2SO_4 as catalyst.

$$2C_2H_5OH \xrightarrow{\text{conc. } H_2SO_4} C_2H_5OC_2H_5 + H_2O$$

3. Hydrolysis of esters using H_2SO_4 as catalyst.

$$\underset{\text{Ethyl ethanoate}}{CH_3COOC_2H_5} + H_2O \overset{H_2SO_4}{\rightleftharpoons} \underset{\text{Ethanoic acid}}{CH_3COOH} + \underset{\text{Ethanol}}{C_2H_5OH}$$

When the catalyst exists in a different phase from that of reactants, it is said to be **heterogeneous catalyst** and the catalysis is called **heterogeneous catalysis.** For example, SO_2 can be oxidized to SO_3 using vanadium pentoxide (V_2O_5) as catalyst.

$$2SO_2 + O_2 \xrightarrow{V_2O_5} 2SO_3$$

Here, V_2O_5 is solid, while the reactants are gaseous. This reaction is employed during the manufacture of sulphuric acid by Contact process.

In heterogeneous catalysis, the catalyst is generally solid while the reactants are gases and the reaction starts from the surface of the solid catalyst. That is why heterogeneous catalysis is also called **surface catalysis.**

Some more examples of industrially important heterogeneous catalytic reactions are :

1. Manufacture of NH_3 from N_2 and H_2 by Haber's process, using iron as catalyst.

$$N_2 + 3H_2 \xrightarrow{Fe} 2NH_3$$

2. Manufacture of CH_3OH from CO and H_2 using ($ZnO + Cr_2O_3$) as catalyst.

$$CO + 2H_2 \xrightarrow[\text{Heat}]{ZnO\text{-}Cr_2O_3} CH_3OH$$

3. Oxidation of NH_3 with O_2 using Pt as catalyst in Ostwald process.

$$4NH_3 + 5O_2 \xrightarrow[\text{Heat}]{Pt} 4NO + 6H_2O$$

4. Oxidation of CO in automobile exhaust by platinum catalyst.

$$2CO + O_2 \xrightarrow{Pt} 2CO_2$$

5. Hydrogenation of oils to form vegetable ghee using finely divided nickel as catalyst.

$$\text{Oil} + H_2 \xrightarrow{Ni} \text{Vegetable ghee}$$

6. Polymerization of ethylene using $TiCl_3$ and trialkyl aluminium (Ziegler-Natta method) as catalyst.

The role of heterogeneous catalyst in increasing the rate of the reaction can be explained in terms of adsorption of the reactants on the surface of the catalyst. Adsorption helps the reactants in the following ways :

(*i*) The simultaneous adsorption of reactants results in increased concentration conditions at the surface of the catalyst and hence the reactions takes place more rapidly at the surface of the catalyst.

(*ii*) Adsorption of reactant molecules makes the attack of other molecules on it more probable because the adsorbed molecule are not free to move about and escape collisions.

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(*iii*) Adsorbed molecules may expose their sensitive part for reaction with other molecules.

(*iv*) During chemisorption large amount of heat is produced as heat of adsorption. This may supply the activation energy required for the reaction.

(*v*) As a result of adsorption, dissociation of adsorbed molecules may take place resulting in the formation of reactive atoms or free radicals. For example, in the reactions involving H_2 and metallic catalyst (Ni, Pt or Pd), hydrogen molecule splits up into atoms at the surface of catalyst.

Nature of Solid Catalysts

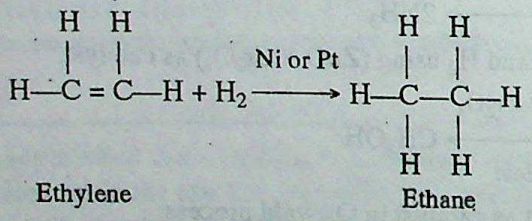
Solid catalysts may be the substances such at metals, alloys of metals, metal oxides, metal sulphides, etc. They may be pure substances or mixtures of substances.

Two important aspects of the solid catalysts are *activity* and *selectivity.*

(*a*) **Activity.** *The ability of catalysts to accelerate the rates of chemical reactions* is called **activity.** Catalysts can accelerate the rates of reactions to a very large extent. In some cases, the rates of reactions have been found to increase by the extent of 10^{10} times by the use of catalyst. For example, a mixture of pure hydrogen and pure oxygen does not react at all in the absence of catalyst, however, in the presence of platinum as catalyst the mixture reacts with explosive violence to form water.

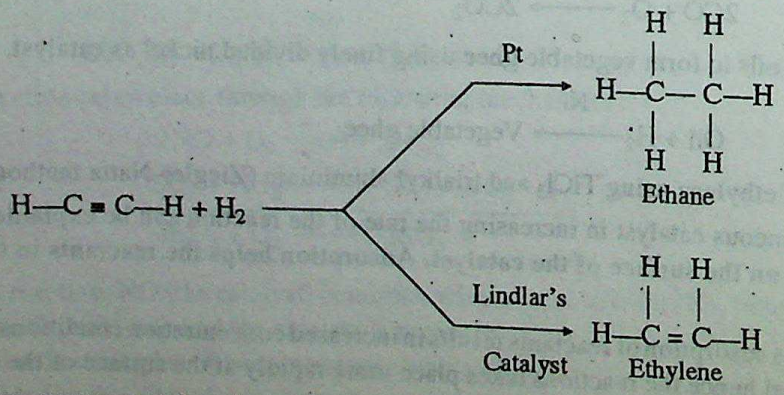
$$2H_2 + O_2 \xrightarrow{Pt} 2H_2O$$

Similarly, the hydrogenation of ethylene to form ethane does not take place at all in the absence of a catalyst. However, in the presence of finely divided metal such as nickel, platinum or palladium, the reaction occurs at room temperature.



It may be noted that the granular forms of the solid catalyst have large surface area. Hence, they are more active than the bulk forms.

(*b*) **Selectivity.** *It is the ability of the catalyst to direct a reaction to yield a particular product.* For example, acetylene on reaction with H_2 in the presence of Pt as catalyst gives ethane while in the presence of Lindlar's catalyst (Palladium, partially inactivated by quinoline or heavy metal ions) it gives ethylene.



A heterogeneous catalysed reaction involves several steps. The initial step is usually chemisorption of reactants on the surface of the catalyst. The places at the surface where reacting molecules may become

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adsorbed are called **active sites.** The adsorbed reactants then undergo diffusion, dissociation and chemical reaction at the surface. Finally, the products formed undergo desorption.

Shape-selective Catalysis by Zeolites

Zeolites are microporous aluminosilicates of the general formula

$$M_{x/n}\,[(AlO_2)_x(SiO_2)_y].\ m\ H_2O$$

where n is the valency of the metal cation, M^{n+}. Zeolites possess high porosity due to the presence of one-, two- or three-dimensional networks of interconnected channels and cavities of molecular dimensions. Zeolites are widely used as catalyst in petro-chemical industry for cracking and isomerization of hydrocarbons. The important feature of zeolite catalysis is shape selectivity. The catalytic activity of zeolites depends upon the size of the cavities (cages) and pores (apertures) present in them. The pore size in zeolites is generally in the range 260-740 pm. Molecules of appropriate sizes may be trapped in the cavities and it is this property that makes possible their use as selective adsorbents. Depending upon the sizes of reactant and product molecules relative to the sizes of cavities and apertures of the zeolite, reactions proceed in a specific manner.

Alcohols are converted into gasoline using a zeolite catalyst ZSM-5. ZSM-5 has the formula

$$H_x[(AlO_2)_x\,(SiO_2)_{96-x}].\ 16H_2O$$

The alcohol is dehydrated in the cavities by the protons and hydrocarbons are formed. The shape selectivity in this reaction can be observed from the data given below for the conversion of method and 1-heptanol to mixture of hydrocarbons.

Product	*Starting from methanol (CH_3OH) (per cent)*	*Starting from 1-heptanol (per cent)*
Methane	1.0	0.0
Ethane	0.6	0.3
iso-Butane	18.7	19.3
n-Butane	5.6	11.0
iso-Pentane	7.8	8.7
Benzene	1.7	3.4
Toluene	10.5	14.3
Xylenes	17.2	11.6

The composition of the product mixture depends upon the ability of the cavities in zeolite to accommodate normal and *iso*-alkanes as well as benzene and its derivatives.

IMPORTANT TERMS AND CONCEPTS

- **Adsorption.** Presence of a substance in higher concentration at the surface than the adjoining bulk phases.
- **Adsorbent.** The substance on the surface of which adsorption takes place.
- **Adsorbate.** The substance which is present in higher concentration at the surface of adsorbent.
- **Physisorption.** In this type of adsorption adsorbate is held on the surface of adsorbent by van der Waal's forces.
- **Chemisorption.** In this type of adsorption adsorbate is held on the surface of adsorbent by chemical bonds.

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- **Enthalpy of Adsorption.** Enthalpy change accompanying the adsorption of one mole of adsorbate on the adsorbent. Enthalpy of adsorption is always negative.
- **Extent of Adsorption** decreases with increase in temperature and increases with increases in pressure.
- **Adsorption Isotherm.** A graph of extent of adsorption vs. pressure at constant temperature.
- **Freundlich Adsorption Isotherm**

$$\frac{x}{m} = kp^{1/n}\ ;\ \log\frac{x}{m} = \log k + \frac{1}{n}\log p$$

- **Adsorption Isobar.** A graph of extent of adsoption vs. temperature at constant pressure.
- **Saturation Pressure.** The pressure beyond which extent of adsorption becomes independent of pressure.
- **Colloidal State.** A state in which the particle size of the substance is in the range 1 – 1000 nm.
- **Sol.** A colloidal solution containing solid as the disperse phase and liquid as the dispersion medium.
- **Lyophilic Sol.** A colloidal solution in which there is great affinity between the disperse phase and the dispersion medium.
- **Lyophobic Sol.** A colloidal solution in which there is little affinity between the disperse phase and the dispersion medium. Lyphobic sols are less stable.
- **Macrmolecular Colloid.** A colloid in which colloidal particles are macromolecules.
- **Multimolecular Colloid.** A colloid in which colloidal particles are clusters or aggregates of smaller molecules.
- **Associated Colloid.** A colloid which is formed when concentration of the solute exceeds a limit.
- **Peptization.** Preparation of a colloidal solution by shaking the substance with dispersion medium in the presence of some suitable electrolyte.
- **Coagulation.** Precipitation of a colloidal solution by induced aggregation of colloidal particles.
- **Coagulation Value.** Minimum concentration of the electrolyte in millimoles per litre needed to cause coagulation of the sol.
- **Hardy-Shulze Rules.** In case of electrolytes, the ion carrying charge opposite to that of colloidal particles is effective in causing coagulation. Greater the valency of the ion causing the coagulation greater is the coagulating power.
- **Brownian Movement.** The zig-zag movement of colloidal particles.
- **Tyndall Effect.** Scattering of light by colloidal particles.
- **Electrophoresis.** The movement of colloidal particles towards one of the electrodes on passage of electricity through colloidal solution.
- **Gold Number.** A parameter used for expressing protective power of a lyophilic colloid.
- **Catalysis.** Acceleration of rate of a reaction by using some additional substance.
- **Heterogenous Catalysis.** Surface catalysis. Acts through adsorption.
- **Zeolites.** Shape selective catalysts.

EXERCISES

VERY SHORT ANSWER QUESTIONS
(1 Mark)

1. What name is generally given to a phenomenon when absorption also occurs along with adsorption ?
2. Out of carbon monoxide and ammonia which is adsorbed on activated charcoal to a large extent and why ?

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3. On passing H_2S through dilute HNO_3 the colourless solution becomes turbid. Why ?
4. What name can be given to a sol in which dispersion medium is benzene ?
5. A sol is prepared by addition of excess of $AgNO_3$ solution in KI solution. What charge is likely to develop on the colloidal particles ?
6. If we add equimolar amounts of ferric hydroxide sol and arsenic sulphide sol, what will happen ?
7. What is meant by the term critical micellization concentration (CMC) ?
8. What is the function of emulsifying agent ?
9. What is a syneresis ?
10. Are the sols of metal in water hydrophilic or hydrophobic ?
11. Does colloid refer to some specific substance or the state of a substance ?
12. What is observed when a beam of light is passed through a colloidal solution of arsenious sulphide ? *[A.I. CBSE (O) 1992]*
13. How does adsorption of a gas on a solid surface vary with temperature ? *[CBSE (1) 1992]*
14. What is an adsorption isotherm ? *[CBSE (2) 1992]*
15. What are micelles ? Give an example of micellar system. *[CBSE (4) 1992]*
16. Give one example each of *oil in water* and *water in oil* emulsions.
17. What are aerosols ?
18. Why adsorption is always exothermic ?
19. Define gold number and coagulation value.
20. What is adsorption isobar ?
21. Give one example each of positively charged sol and negatively charged sol.
22. What is demulsification ?
23. Define specific surface area.
24. What is difference between sols and gels ?
25. Give mathematical expression for Freundlich adsorption isotherm.
26. Draw adsorption isobars for chemisorption and physisorption.

DESCRIPTIVE QUESTIONS
(2 or 3 Marks)

Adsorption

27. Write a short note on adsorption. How does it differ from adsorption ?
28. What are the differences between physisorption and chemisorption ? *(P.S.E.B 1991)*
29. On what factors does adsorption of gases on solids depend ?
30. What are isotherms and isobars ? What is the difference between isotherms of physisorption and chemisorption ?
31. State the following :
    (*i*) Adsorbent (*ii*) Adsorbate (*iii*) Adsorption.
32. How does extent of adsorption depend upon surface area of the adsorbent ?
33. What do you understand by activation of adsorbent ? How is it achieved ?
34. What are the applications of adsorption ?
35. What role does adsorption play in heterogeneous catalysis ?

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Colloids

36. Write a short note on colloids. Do they belong to a particular class of compounds ?
37. Give two chemical methods for the preparation of colloids.
38. Give two physical methods for the preparation of colloids.
39. "Thomas Graham's classification of the substances into *colloids* and *crystalloids* has been found to be wrong." Comment upon the statement.
40. How are the colloidal solutions classified on the basis of dispersed phase and dispersion medium ?
41. What do you understand by lyophilic and lyophobic colloids ? How will you distinguish between them ?
42. Write brief note on :
    (*i*) Coagulation (*ii*) Gold number (*iii*) Hardy-Schulze law.
43. Explain the following terms :
    (*i*) Lyophobic sols (*ii*) Gold number (*iii*) Peptisation.
44. What is Tyndall effect ? Explain with diagram.
45. How will you prepare a colloidal solution of gold ? How is it stabilised ?
46. Enlist the main applications of colloidal solutions.
47. Compare characteristics of physical adsorption and chemisorption.
48. Enlist the factors which influence the adsorption of gases on solids.
49. How do pressure and temperature influence the adsorption of a gas a on a solid ?
50. Describe Freundlich's adsorption isotherm and explain various symbols used.
51. Give four points of difference between lyophilic and lyophobic colloids.
52. Explain the following terms with suitable examples :
    (*i*) Gel (*ii*) Aerosol (*iii*) Hydrosol.
53. What is the difference between multi-molecular and macro-molecular colloids ? Give one example of each type. How are associated colloids different from these two type of colloids ?
54. What is an emulsion ? Give one example.
55. What is the role played by an emulsifier ?
56. Explain the following in connection with colloids :
    (*i*) Gold number (*ii*) Hardy-Schulze rule.
57. Mention two uses each of colloids and emulsions.
58. What is the difference between a sol and a gel ? What are emulsions ?
59. (*a*) How can a colloidal solution and a true solution of the same colour be distinguished from each other ?
    (*b*) What is demulsification ?
    (*c*) Give two uses of soap as emulsifier.
60. (*a*) Explain reversible and irreversible sols with examples.
    (*b*) What is peptisation ?
61. Explain what happens when :
    (*a*) beam of light is passed through colloidal solution of As_2S_3.
    (*b*) sodium hydroxide is added to ferric hydroxide sol.
    (*c*) an electrical current is passed through a colloidal solution.
62. How will you distinguish between physical adsorption and chemical adsorption ?
63. Write the mathematical form of Freundlich adsorption isotherm and explain the various symbols used therein.

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64. What are emulsions ? Give one example each of water-in-oil type and oil-in-water emulsions.

65. Explain what is observed when a colloidal solution of arsenious sulphide is treated as follows :

(*i*) A beam of light is passed through it (*ii*) An electrolyte is added to it

(*iii*) It is brought under the influence of electric field. [*A.I. CBSE (O) 1988*]

66. Comment on the statement that "Colloid is not a substance but a state of substance". [*A.I. CBSE (O) 1989*]

67. Explain the term *Brownian movement* and *Peptisation.* [*A.I. CBSE (O) 1990*]

68. What are lyophobic and lyophilic sols ? Compare the two in terms of stability and reversibility. [*A.I. CBSE (O) 1991*]

69. Define the following :

(*i*) Adsorbent (*ii*) Adsorbate (*iii*) Desorption.

70. Differentiate between multi-molecular and macromolecular colloids. Give one example of each.

71. Explain any two of the following :

(*i*) Gold number (*ii*) Dialysis (*iii*) Tyndall effect.

72. Give two examples of heterogeneous catalytic reactions. What is the role of adsorption in such reactions ?

73. What do you understand by *activity* and *selectivity* of catalysts ?

74. (*a*) Justify the use of gelatin as protective colloid.

(*b*) How does the theory of selective adsorption explain the origin of charge on colloidal particle ?

75. Explain the term *shape selective catalysis* and *emulsion* with one example each. [*A.I. CBSE (O) 1991*]

76. What are zeolites ? Describe some of their features. [*A.I. CBSE (O) 1992*]

77. What happens when a freshly precipitated $Fe(OH)_3$ is shaken with little amount of dilute solution of $FeCl_3$? (*Har. S.B. 1992*)

78. What is the difference between multi-molecular and macromolecular colloids ? Give one example of each type. How are associated colloids different from these two types of colloids ? (*CBSE 1993*)

79. Describe the following terms while stating the properties of colloids :

(*i*) Brownian movement (*ii*) Tyndall Effect (*iii*) Electrophoresis. (*A.I. CBSE 1994*)

80. Describe a chemical method each for the preparation of sols of sulphur and platinum in water. (*A.I. CBSE 1995*)

81. What are multimolecular and macromolecular colloids ? (*CBSE 1995*)

82. Differentiate between the following pairs

(*i*) Sols and Emulsions (*ii*) Physical adsorption and Chemical adsorption

(*iii*) Lyophobic sols and Lyophilic sols. (*Har. S.B. 1995*)

83. What do you understand by adsorption isotherm and adsorption isobar ? Explain Freundlich adsorption isotherm for the adsorption of gases on solids. (*Pb. S.B. 1995*)

84. What are micelles ? Give an example of micellar system. (*C.B.S.E. 1997*)

85. Name two industrial processes in which catalysis are employed. (*C.B.S.E. 1997*)

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select the correct answer in questions from 1 to 26 :

1. An emulsion is a colloidal system of
   (*a*) two solids (*b*) two liquids
   (*c*) one gas and one solid (*d*) one gas and one liquid.
2. Which of the following is a lyophobic colloid ?
   (*a*) gelatin (*b*) sulphur (*c*) starch (*d*) gum arabic.
3. The nature of bonding forces in adsorption are
   (*a*) purely physical such as van der Waal's forces (*b*) purely chemical
   (*c*) both chemical and physical (*d*) sometimes physical and sometimes chemical.
4. The protective power of a lyophilic sol is
   (*a*) defined by Hardy-Schulze rule (*b*) proportional to the quantity of electrical charge on it
   (*c*) measured in terms of gold number (*d*) determined by the size of its colloidal particles.
5. The Tyndall effect associated with colloidal particles is due to
   (*a*) presence of electrical charge (*b*) scattering of light
   (*c*) absorption of light (*d*) reflection of light.
6. Which one of the following is not applicable to chemisorption ?
   (*a*) Its heat of adsorption is high (*b*) It takes place at high temperature
   (*c*) It is reversible (*d*) It forms mono-molecular layers.
7. In the colloidal state the particle size ranges
   (*a*) below 1 nm (*b*) between 1 nm to 100 nm
   (*c*) more than 100 nm (*d*) none of the above.
8. All colloids
   (*a*) are suspensions of one phase in another (*b*) are two-phase systems
   (*c*) contain only water-soluble particles (*d*) are true solutions.
9. Colloids can be purified by
   (*a*) condensation (*b*) peptization (*c*) coagulation (*d*) dialysis.
10. Milk is an example of
    (*a*) emulsion (*b*) suspension (*c*) foam (*d*) sol.
11. Colloidal particles in a sol can be coagulated by
    (*a*) heating (*b*) adding an electrolyte
    (*c*) adding oppositely charged sol (*d*) any of the above methods.
12. Emulsifier is an agent which
    (*a*) accelerates the dispersion (*b*) homogenizes an emulsion
    (*c*) stabilizes an emulsion (*d*) aids the flocculation of an emulsion.
13. Fog is a colloidal system of
    (*a*) gas in liquid (*b*) liquid in gas (*c*) gas in gas (*d*) gas in solid.

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14. Given below are a few electrolytes, indicate which one among them will bring about the coagulation of a gold sol quickest and in the least of concentration ?
(*a*) NaCl (*b*) $MgSO_4$ (*c*) $Al_2(SO_4)_3$ (*d*) $K_4[Fe(CN)_6]$.

15. Milk is an emulsion of fat, etc., dispersed in
(*a*) water (*b*) amino acid (*c*) fatty acid (*d*) saline water.

16. When a colloidal solution is observed under ultramicroscope, we can see
(*a*) light scattered by colloidal particle (*b*) size of the colloidal particle
(*c*) shape of the colloidal particle (*d*) relative size of the colloidal particle.

17. Colloidal solutions are classified on the basis of
(*a*) molecular size (*b*) organic or inorganic (*c*) surface tension value (*d*) pH value.

18. Gel is a system of
(*a*) solid dispersed in liquid medium (*b*) solid dissolved in liquid medium
(*c*) liquid dispersed in liquid medium (*d*) liquid dispersed in solid medium.

19. Gold number gives an indication of
(*a*) protective nature of colloids (*b*) purity of gold in suspension
(*c*) the charge on a colloidal solution of gold (*d*) *g*-mole of gold per litre.

20. The electrical charge on a colloidal particle is indicated by
(*a*) Brownian movement (*b*) electrophoresis (*c*) ultra microscope (*d*) molecular sieves.

21. The minimum concentration of an electrolyte required to cause coagulation of a sol is called
(*a*) flocculation value (*b*) gold number (*c*) protective value (*d*) none of these.

22. Cottrell precipitator works on the principle of
(*a*) distribution law (*b*) neutralization of charge on colloids
(*c*) Le-Chatelier's principle (*d*) addition of electrolytes.

23. A dispersion of silver chloride in water is
(*a*) hydrophilic colloid (*b*) an emulsion (*c*) alcosol (*d*) hydrophobic colloid.

24. Which one of following statements is not correct in respect of lyophilic sols ?
(*a*) There is a considerable interaction between the dispersed phase and dispersion medium.
(*b*) These are quite stable and are not easily coagulated.
(*c*) They carry charge. (*d*) The particle are hydrated.

25. As_2S_3 sol is
(*a*) Positive colloid (*b*) Negative colloid (*c*) Neutral colloid (*d*) None of the above.

26. Crystalloids differ from colloids mainly in respect of
(*a*) Electrical behaviour (*b*) Particle nature (*c*) Particle size (*d*) Solubility.

FILL IN THE BLANKS

1. The substance on whose surface adsorption takes place is called an .....
2. Removal of adsorbate from the surface of adsorbent is called .....
3. Migration of colloidal particles under the effect of electric field is called .....
4. The heat of adsorption in case of physisorption is about .....
5. The phenomenon of zig-zag motion of colloidal particles is known as .....

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6. Smoke is a colloidal solution of ..... in .....
7. Lyophilic sols are ..... stable than lyophobic sols.
8. Electrical properties of a colloidal solution are demonstrated by .....
9. Tyndall effect takes place due to ..... of light by colloidal particles.
10. Protective power of a lyophilic sol is expressed in terms of .....
11. The liquid-liquid colloidal dispersions are called ..... *(A.I. CBSE 1995)*

TRUE/FALSE STATEMENTS

Which of the following statements are true and which are false :

1. Physisorption is non-specific.
2. Chemisorption needs activation energy.
3. A graph of x/m *vs* temperature at constant pressure is called adsorption isotherm.
4. Suspensions have solute particles with size less than 1 nm.
5. $Fe(OH)_3$ sol contains positively charged colloidal particles.
6. Chemisorption is irreversible.
7. Adsorption isobars of chemisorption and physisorption are of the same type.
8. Milk is an example of *water in oil* emulsions.
9. Gold sol can be prepared by Bredig's arc method.
10. Gel is a system in which liquid is the dispersed phase and solid is the dispersion medium.

MATCHING TYPE QUESTIONS

Match the items of column A with that given in column B :

Column A	Column B
1. A negatively charged sol	1. Gold number
2. A macromolecular colloid	2. As_2S_3 sol
3. A positively charged sol	3. Starch sol
4. Protecting power of a lyophilic colloid	4. $Fe(OH)_3$ sol
5. Cheese	5. an emulsion
6. Cod liver oil	6. a Gel

HINTS AND ANSWERS

VERY SHORT ANSWER QUESTIONS

1. Such phenomenon is called *sorption.*
2. Ammonia ; because more easily liquifiable gas undergoes adsorption to a greater extent.
3. It is due to the formation of colloidal sol of sulphur.
4. Benzosol.
5. Positive ; there will be adsorption of Ag^+ by the colloidal particles (AgI. Ag^+).

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6. Both the sols will get coagulated.
7. The minimum concentration of electrolyte required for micelle formation.
8. The emulsifying agent diminishes the surface tension and thus stabilises the emulsion. For example, soap acts as emulsifying agent in getting emulsion of oil in water.
9. When gels are kept undisturbed for some time, they give out water/liquid without undergoing any contraction in gel volume. This is known as *syneresis*.
10. Hydrophobic.
11. State of substance because same substance can act as crystalloid as well as colloid in different solvents.
12. Path of the light becomes visible due to scattering of light (*Tyndall effect*) by colloidal particles.
13. It decreases with increase in temperature.
16. Milk, cod-liver oil.

MULTIPLE CHOICE QUESTIONS

1. (*b*)	2. (*b*)	3. (*c*)	4. (*c*)	5. (*b*)	6. (*c*)
7. (*b*)	8. (*b*)	9. (*d*)	10. (*a*)	11. (*d*)	12. (*c*)
13. (*b*)	14. (*c*)	15. (*a*)	16. (*a*)	17. (*a*)	18. (*d*)
19. (*a*)	20. (*b*)	21. (*a*)	22. (*b*)	23. (*d*)	24. (*b*)
25. (*b*)	26. (*c*).				

FILL IN THE BLANKS

1. adsorbent	2. desorption	3. electrophoresis
4. 20 – 40 kJ mol^{-1}	5. Brownian movement	6. solid, gas
7. more	8. electrophoresis	9. scattering
10. Gold number	11. Emulsions.	

TRUE/FALSE STATEMENTS

1. True	2. True	3. False	4. False	5. True	6. True
7. False	8. False	9. True	10. True.		

MATCHING TYPE QUESTIONS

1—2, 2—3, 3—4, 4—1, 5—6, 6—5.

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16

Biomolecules : Structure and Function

LEARNING OBJECTIVES

In this Unit, we shall learn about

- *Carbohydrates : monosaccharides, disaccharides, polysaccharides.*
- *Amino acids. Peptides—structure and classification.*
- *Proteins : structure and their role.*
- *Nucleic acids—DNA and RNA.*
- *Biological functions of nucleic acids—protein synthesis and replication.*
- *Lipids—structure, membranes and their functions.*

All living systems need matter as well as energy in one form or the other for their growth and maintenance. The bodies of living systems can be compared to factories. Just as factories require *fuels* for liberation of energy and *machines* for the proper utilisation of energy, the living systems also require fuels and machines. Food constitutes fuel for living beings and enzymes act as machines. The major constituents of food are *carbohydrates, fats* and *proteins.* The enzymes help in the conversion of food into body parts through the series of chemical processes which are also called *biological reactions.* ***The branch of science that deals with the study of the chemical composition and the structure of living organisms and also various chemical changes taking place within them*** is called **biochemistry.** The complex organic molecules which form the basis of life, *i.e.*, which build up living organisms and are also required for their growth and maintenance are called **biomolecules.** In this unit, we shall study the structure and function of some of the important biomolecules.

16.1. CARBOHYDRATES

Carbohydrates constitute an important class of compounds like glucose, fructose, sucrose, starch, cellulose, etc., which play a vital role in our everyday life. Originally, the name carbohydrate was given to the compounds pertaining to general formula $C_x(H_2O)_y$, and they were considered to be hydrates of carbon. However, this definition could not hold ground for long due to following reasons :

(*i*) Many compounds like *formaldehyde* (CH_2O), *acetic acid* ($C_2H_4O_2$), etc., conform to formula $C_x(H_2O)_y$ but they do not exhibit the characteristic properties of carbohydrates.

(*ii*) Some carbohydrates like *rhamnose* ($C_6H_{12}O_5$), *deoxyribose* ($C_5H_{10}O_4$) do not conform to the formula $C_x(H_2O)_y$, and

(*iii*) Carbon is not known to form hydrates.

The above facts ultimately gave way to the modern definition of carbohydrates. **Carbohydrates** are now defined as ***polyhydroxy aldehydes or polyhydroxy ketones or the compounds which can be hydrolysed to them.***

Classification of Carbohydrates

Carbohydrates are classified into three different categories depending upon their behaviour towards hydrolysis :

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1. Monosaccharides. *These are simple carbohydrates which cannot be hydrolysed to still simpler carbohydrates.* Glucose and fructose are common examples.

2. Oligosaccharides. *These are the carbohydrates which on hydrolysis give two to nine units of monosaccharides.* Accordingly, they may be further divided into *di, tri* or *tetrasaccharides* depending upon the actual number of monosaccharide units formed by the hydrolysis of a particular oligosaccharide.

Disaccharides give two units of monosaccharides on hydrolysis. Common examples are sucrose and maltose. Both have molecular formula $C_{12}H_{22}O_{11}$.

Trisaccharides give three units of monosaccharides on hydrolysis. Raffinose, $C_{18}H_{32}O_{16}$ is a common example.

Tetrasaccharides give four units of monosaccharides on hydrolysis. Stachyose, $C_{24}H_{42}O_{21}$ is a common example.

3. Polysaccharides. *These are the carbohydrates which are polymeric molecules and can be hydrolysed to give large number of monosaccharide units.* The commonly occurring polysaccharides have the general formula $(C_6H_{10}O_5)_n$. The common examples are starch, glycogen and cellulose.

It may be noted that the carbohydrates which are sweet in taste are collectively called **sugars** while those which are not sweet are called **non-sugars.** *Monosaccharides and disaccharides are* **sugars** *but polysaccharides are* **non-sugars.**

The relative degree of sweetness of various sugars is given below in tabular form

Sugar	Lactose	Maltose	Galactose	Glucose	Sucrose	Fructose
Relative Sweetness	16	32	32	74	100	173

*It may be noted that besides carbohydrates, some other compounds are far more sweet. For example,

Saccharin is about 500 times as sweet as sucrose.

Aspartame, a peptide, is about 160 times sweeter than sucrose.

Monallelin, a protein is about 2000 times sweeter than sucrose.

Monosaccharides

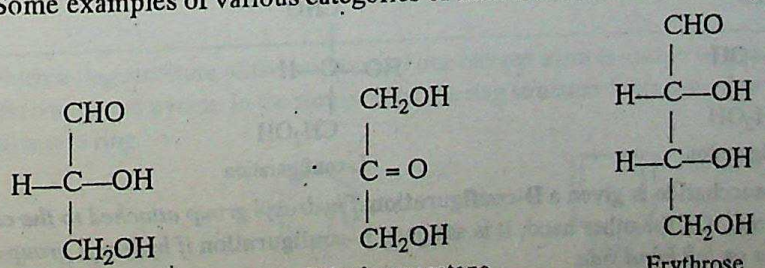
As pointed out earlier, these are the simplest carbohydrates and cannot be hydrolysed to give still simpler carbohydrates. Monosaccharides containing *aldehyde group* are called **aldoses** which those containing *ketonic group* are called **ketoses.** They can be further classified into different categories depending upon the numbers of carbon atoms.

For example,

Monosaccharides with *three* carbon atoms are called **trioses.**

Monosaccharides with *four* carbon atoms are called **tetroses.**

Monosaccharides with *five, six seven* carbon atoms are called **pentoses, hexoses** and **heptoses** respectively. Some examples of various categories of monosaccharides are being given below :



Glyceraldehyde (Aldotriose) — Dihydroxyacetone (Ketotriose) — Erythrose (Aldotetrose)

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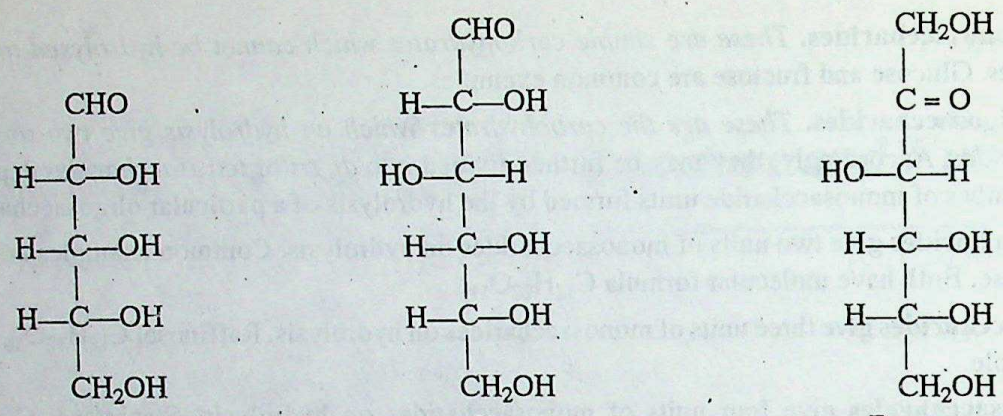
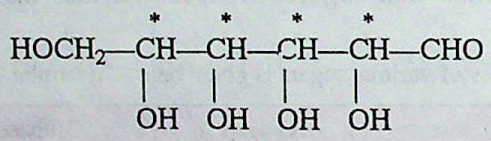
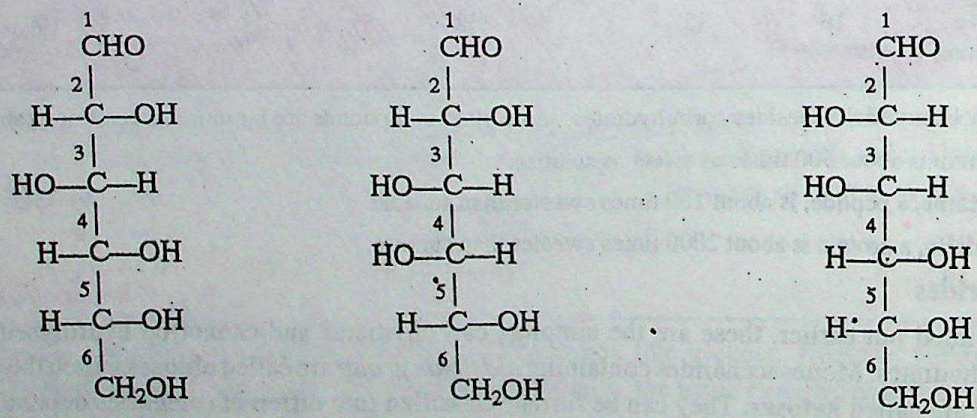


Ribose (**Aldopentose**) Glucose (**Aldohexose**) Fructose (**Ketohexose**)

On carefully examining the monosaccharide molecules, we can realise that they contain one or more chiral carbon atoms. For example, aldohexoses contain four chiral carbons and therefore, $(2)^4$, *i.e.*, 16 optically active isomers should be possible. Three of these sixteen aldohexoses which occur widely in nature are D-glucose, D-galactose and D-mannose whose open chain structure formulae are given as follows :





*D-Glucose D-Galactose D-Mannose

It has been found that these sugars generally exist in the form of cyclic hemiacetal structures. Only a very small number of molecules exist in the form of open chain structure.

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*The letter D before the name of monosaccharides does not refer to dextrorotatory, but represents the configuration as derived from glyceraldehyde. Glyceraldehyde can be represented by two enantiomeric as shown below :

D-configuration L-configuration

By convention a monosaccharide is given a **D-configuration** *if hydroxyl group attached to the carbon adjacent to* $—CH_2OH$ *is on right hand side.* On the other hand, it is assigned **L-configuration** *if hydroxyl group attached to the carbon adjacent to* $—CH_2OH$ *is on left hand side.*

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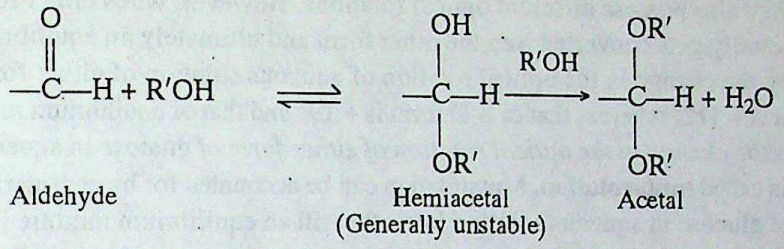
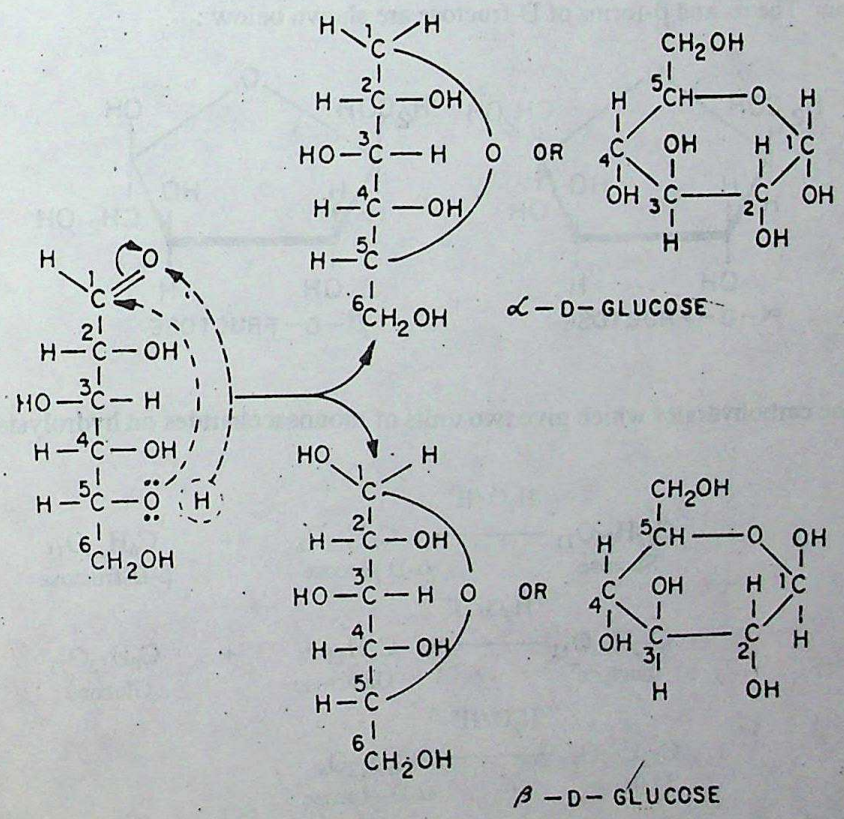
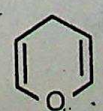
In **unit 8,** we have studied the reaction between aldehydes and alcohols to form hemiacetals and acetals.



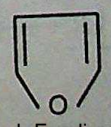
The formation of hemiacetal and acetal as described above is intermolecular in nature, *i.e.*, it involves different molecules. However, in long chain polyhydroxy aldehydes, there is an opportunity of *intramolecular* hemiacetal formation which leads to the cyclic structure. For example, in **glucose** —OH group of (C_5) reacts with carbonyl carbon to form a ring structure consisting of *five carbon* atoms and *one oxygen atom**. As a result of cyclisation, the carbonyl carbon (C_1) also becomes chiral carbon atom and has two possible arrangements of H and OH groups around it. These two arrangements of glucose which differ only in the orientation of hydroxyl groups at C_1 are called **anomers** and are represented as **α-D-glucose and β-D-glucose.** The carbon C_1 is called **annomeric carbon atom.**



*Such a ring structure of five carbon and one oxygen atom is said to be **pyranose** ring. It gets its name from the heterocyclic compound pyram. In the similar way, the ring structure containing four carbon atoms and one oxygen atom is called **furanose** ring.



Pyran



Furan

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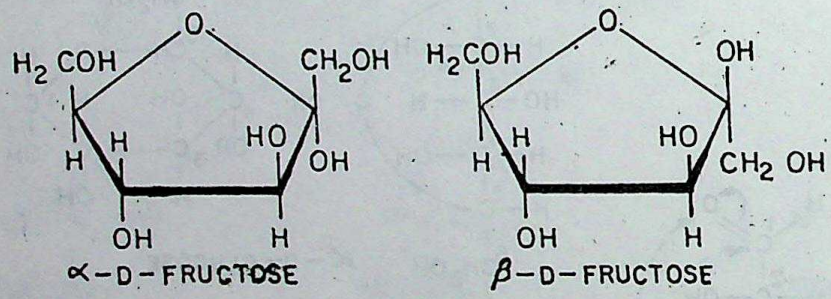
The two forms of glucose, *i.e.*, α-D- and β-D-Glucose exist in different crystalline forms and have different melting points. They also possess different optical rotations. However, when either form of glucose is dissolved in water, it gradually gets converted into the other form and ultimately an equilibrium mixture is formed. This is indicated by the change in the optical rotation of aqueous solution of either form of glucose. Optical rotation of α-D form is + 112° whereas that of β-D form is + 19° and that of equilibrium mixture is + 52°. *The process which involves the change in the optical rotation of either form of glucose* in aqueous *solution to that of equilibrium mixture* is called **mutarotation.** Mutarotation can be accounted for by considering the gradual conversion of either form of glucose in aqueous solution into other till an equilibrium mixture is formed. This process of conversion of one anomeric form of glucose into the other in aqueous solution occurs through the open chain structure. The equilibrium mixture also contains a small amount of open chain form. For example,

α-D-Glucose	$\rightleftharpoons$	**Open chain form**	$\rightleftharpoons$	**β-D-Glucose**
Specific rotation = + 112°		Specific rotation of equilibrium mixture = + 52°		Specific rotation = + 19°
		1 2 3		4 5 6

Like glucose, **FRUCTOSE** ($CH_2OH.COCHOHCHOHCHOHCH_2OH$) also forms an internal ketal using carbonyl carbon C_2 and OH group of C_5 and exists in the form of five-membered ring of four carbon atoms and one oxygen atom. The α- and β-forms of D-fructose are shown below :



Disaccharides

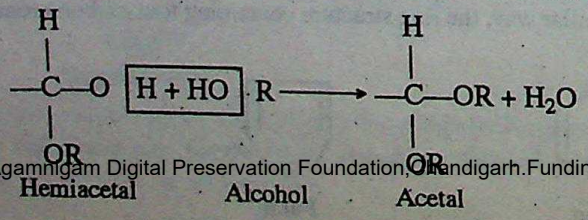
These are the carbohydrates which give two units of monosaccharides on hydrolysis. Some examples are

$$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O/H^+} \underset{\text{α-D glucose}}{C_6H_{12}O_6} + \underset{\text{β-D-fructose}}{C_6H_{12}O_{11}}$$

$$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O/H^+} \underset{\text{Galactose}}{C_6H_{12}O_6} + \underset{\text{Glucose}}{C_6H_{12}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} \xrightarrow{H_2O/H^+} \underset{\text{α-D-glucose}}{2C_6H_{12}O_6}$$

This implies that they are formed by the condensation reaction between two monosaccharides. Just as hemiacetal reacts with alcohol to form acetal and water, in the similar way, the hemiacetals of monosaccharide



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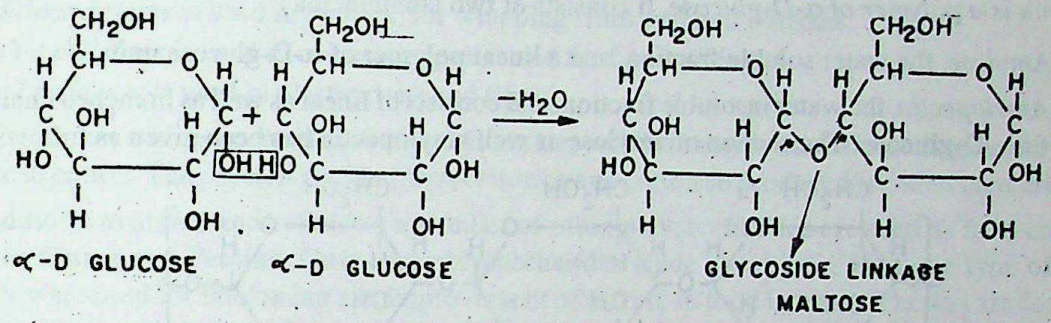
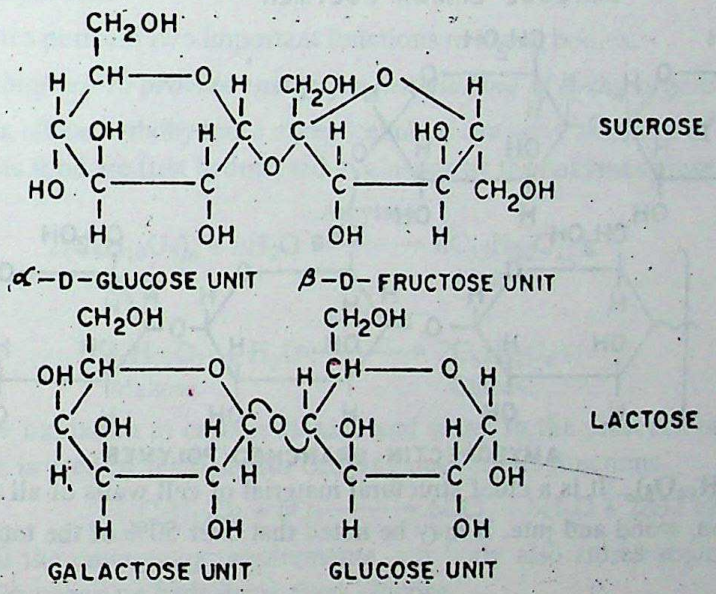
units undergo condensation between their OH groups to form disaccharides. The linkage which holds monosaccharide units in a disaccharide molecule is called **glycoside linkage.**

For example, condensation between two α-*D-glucose* units results in the formation of **maltose***.



Similarly, formation of *sucrose* involves condensation of α-*D glucose* and β-*D fructose* and *lactose* involve condensation of *galactose* and *glucose* units. The formulae of sucrose and lactose are being given as follows :



Inversion of Sugar

Sucrose is *dextro rotatory* with specific rotation + 66.5°. On hydrolysis in the presence of HCl or enzymes *invertase*, it produces mixture of D(+) glucose (specific rotation + 52.7°) and D(–) fructose (specific rotation = – 92.4°). Since specific rotation of D(–) fructose is greater than D(+) glucose, the resulting solution becomes *laevorotatory*. As hydrolysis produces change in optical nature from *dextro rotatory* to *laevorotatory*, the process is called **inversion of sugar.** The mixture of D(+) glucose and D(–) fructose obtained as a result of hydrolysis is called **INVERT SUGAR.** It may be noted that honey is mostly invert sugar as bees produce enzymes *invertase*.

Polysaccharides

These are the carbohydrates which are made of large number of monosaccharide units. They are naturally occurring condensation polymers in which large number of monosaccharide units are joined together through glycoside linkages. They are colourless, tasteless amorphous powders. They play vital role in plant and animal life. Let us study the structure of two important polysaccharides **starch** and **cellulose.**

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*Structures of complex molecules will not be asked for evaluation.

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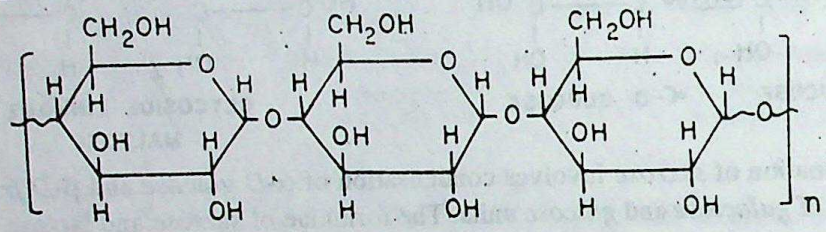
1. **Starch, $(C_6H_{10}O_5)_n$.** It is a most abundant source of carbohydrate in human diet. It is a major food reserve material of plants and occurs mainly in seeds, fruits, tubers and roots of the plants. The important sources of starch are wheat, rice, maize, potatoes, legumes and other vegetables.

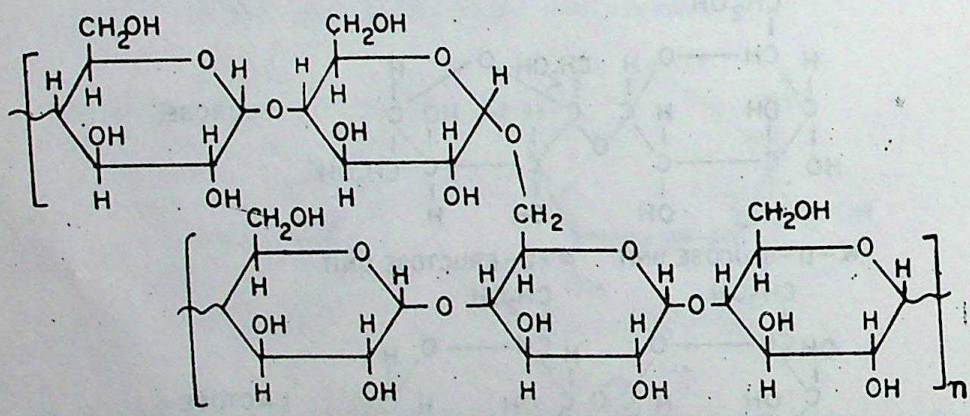
Starch is a polymer of α-D-glucose. It consists of two components :

(*a*) *Amylose,* the water soluble fraction, and a linear polymer of α-D-glucose units.

(*b*) *Amylopectin,* the water insoluble fraction, and consists of linear as well as branched chain polymers of α-D-glucose. The section of amylose as well amylopectin has been given as follows :



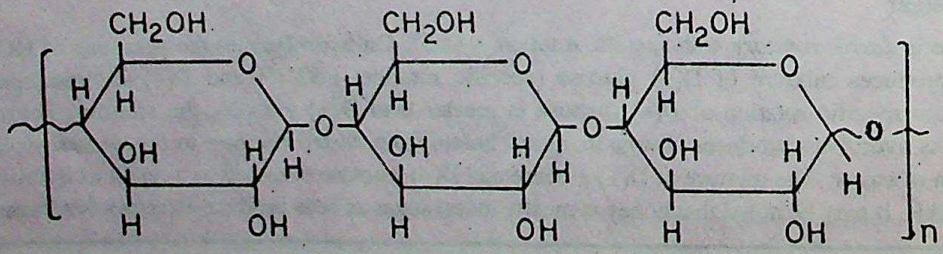
AMYLOSE LINEAR POLYMER



AMYLOPECTIN BRANCHED POLYMER

2. **Cellulose, $(C_6H_{10}O_5)_n$.** It is a chief structural material of cell walls of all the plants. It is also the chief component of cotton, wood and jute. It may be noted that over 50% of the total organic matter of the living world is cellulose.

Structurally, *cellulose is a linear polymer of β-D-glucose* as shown below :



CELLULOSE
(POLYMER OF β-D-GLUCOSE)

The chains are held together by hydrogen bonds between glucose units of adjacent strands. The chains are so arranged as to constitute the bundles.

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Cellulose forms many useful products when treated with suitable chemical reagents. Some of the important products are :

Celluloid, which is used in films.

Gun cotton, which is an explosive.

Cellulose acetate is used in plastics, for wrapping films and nail polishes.

Methyl cellulose is used in cosmetics, pastes and for fabric sizing.

Ethyl cellulose is used in plastic coats and films.

On treatment with concentrated sodium hydroxide, cellulose forms a transluscent mass which imparts a silky lustre to cotton. The process is called *mercerisation* and cotton so produced is called mercerised cotton.

In addition to starch and cellulose, a number of other polysaccharides are used as food components. These are the **Gums** and **Pectins. Gums** are polysaccharides made up of more than one type of monosaccharides. They are used for thickening and improvement of texture in food industry. **Pectins** are found in fruit skins and are extracted by boiling. Jelly preparations contain pectin dissolved in a fruit juice. The pectin causes jelly to set into a semi-solid.

Significance of Carbohydrates

The carbohydrates perform two important functions in living bodies.

(*a*) ***They act as biofuels to provide energy for functioning of living organisms.***

In human system, all the carbohydrates except cellulose can serve as source of energy. Starch and various sugars which are taken as food are first hydrolysed to glucose by the enzymes present in the digestive system.

$$\underset{\text{Starch}}{2(C_6H_{10}O_5)_n} + nH_2O \xrightarrow{\text{Amylase}} \underset{\text{Maltose}}{nC_{12}H_{22}O_{11}}$$

$$\underset{\text{Maltose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Maltase}} \underset{\text{Glucose}}{2C_6H_{12}O_6}$$

Glucose on slow oxidation to carbon dioxide and water in the presence of enzymes liberates large amount of energy which is used by the body for carrying out various functions.

$$C_6H_{12}O_6 + 6O_2 \longrightarrow 6CO_2 + 6H_2O + 2832\ \text{kJ}$$

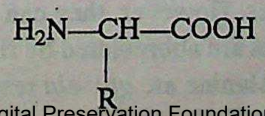
In order to fulfil the emergency requirements, our body also stores some of the carbohydrates as glycogens in the liver. Glycogen on hydrolysis gives glucose.

It may be noted that cellulose cannot be hydrolysed in our body because enzymes required for its hydrolysis are not present in our body. However, grazing animals are capable of hydrolysing cellulose to glucose.

(*b*) ***They act as constituents of cell membrane.***

16.2. AMINO ACIDS

These are amino substituted carboxylic acids. Of various amino acids, the α-amino acids are quite important because they are the building blocks of peptides and proteins. In α-amino acids, the amino group is present on the α-carbon atom (*i.e.* C atom next to COOH group). Thus, they can be represented by the general formula



Group R—is different for different amino acids

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The amino acid, which contain two —COOH groups are called **acidic amino acids** while those containing two NH_2 groups are called **basic amino acids.** For example, *glutamic acid* and aspartic acid are acidic amino acids while *lysine* is basic amino acid.

About 20 of the α-amino acids have been identified as the constituents of most of the animal and plant proteins. The formulae of such amino acids along with their common and abbreviated names have been given in Table 16.1.

Essential and Non-essential Amino acids

Out of 12 amino acids which are required for protein synthesis, the human body can synthesis 10. The amino acids which the body can synthesis are called **non-essential amino acids.** The remaining 10 amino acids which the body is not able to synthesis are called **essential amino acids.** The essential amino acids must be supplied to our bodies through our diet because they are required for proper health and growth. The deficiency of essential amino acids may cause diseases like *Kwashiorkor* in which water balance of the body is disturbed.

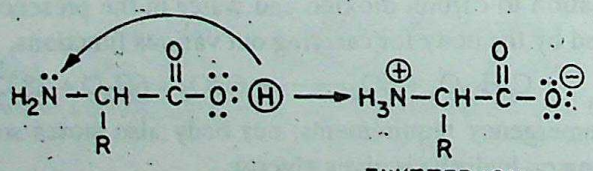
Configuration of α-Amino acids

All α-amino acids except glycine are chiral molecules and exhibit optical activity. The naturally occurring α-amino acids have L-configuration *i.e.* —NH_2 group is on LHS as —OH group in α-glyceraldehyde

L-Glyceraldehyde L-Amino acid

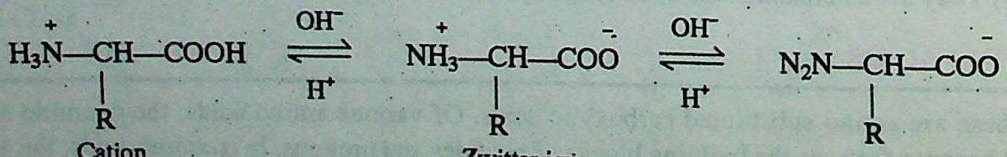
Structure of Amino Acids

It has been found by spectroscopic means that —COOH and —NH_2 groups of amino acids do not exist as such but they react with each other to form *internal salt structure* which is also called **zwitter ion structure.** In the formation of zwitter ion, a proton from —COOH part of the molecule is released and attaches itself to —NH_2 part to constitute a dipolar ion as shown below :



ZWITTER ION

The amino acids are colourless, crystalline and high melting solids. They are moderately soluble in water. In *acidic solution* amino acids exist as *cations* whereas in basic solutions they exist as *anions.* At the intermediate pH, however, they exist as zwitter ion (a dipolar ion).



Cation Zwitter ion Anion

Naming the amino acids

Amino acids are known by their common names. However, they can also be named by following the IUPAC rules. In protein or peptides the amino acid units are abbreviated by first three letters of their common names. For example, the abbreviation for glycine and alanine are *gly, ala* respectively. The names, structure, and abbreviations of various α-amino acids are given in Table 16.1.

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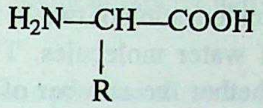
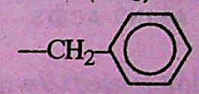
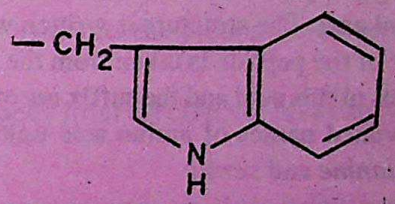
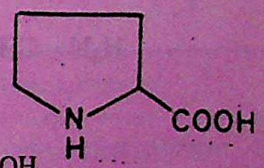
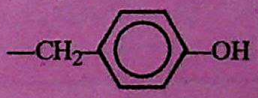
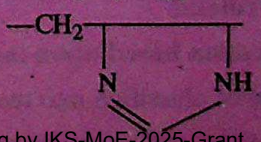
Table 16.1. Structure and Names of Some α-Amino Acids

General Structure



Common name	*Abbreviated name*	*–R*
Glycine	*Gly*	—H
Alanine	*Ala*	
*Valine	*Val*	$—CH(CH_3)_2$
*Leucine	*Leu*	$—CH_2—CH(CH_3)_2$
Isoleucine	*Ileu*	$—CH(CH_3)—CH_2—CH_3$
*Phenylalanine	*Phe*	
*Methionine	*Met*	$—CH_2—CH_2—S—CH_3$
*Tryptophane	*Trp*	
*Proline	*Pro*	
Serine	*Ser*	$—CH_2—OH$
Cysteine	*Cys*	$—CH_2—SH$
Aspargine	*Asn*	$—CH_2—CONH_2$
Glutamine	*Gln*	$—CH_2—CH_2—CONH_2$
Threonine	*Thr*	$—CH(OH)—CH_3$
Tyrosine	*Tyr*	
Acidic amino acids		
Aspartic acid	*Asp*	$—CH_2—COOH$
Glutamic acid	*Glu*	$—CH_2—CH_2—COOH$
Basic amino acids		
*Lysine	*Lys*	$—CH_2—(CH_2)_3—NH_3^+$
Arginine	*Arg*	$—CH_2—(CH_2)_2—NH—C(=NH_2^+)—NH_2$
Histidine	*His*	

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*These are essential amino acids.

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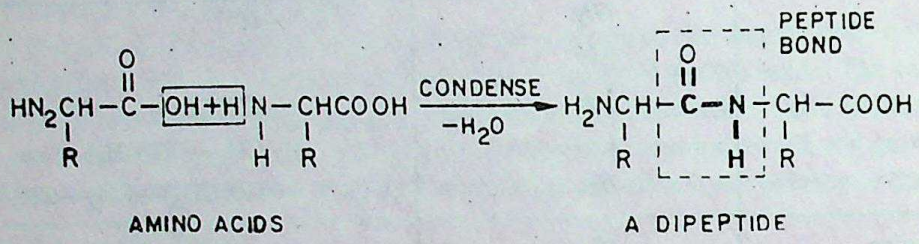
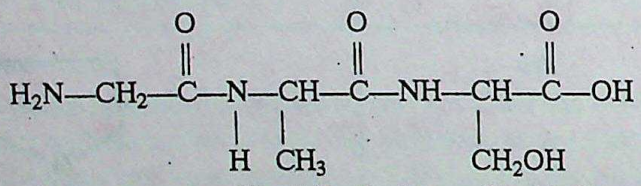
Peptides and Peptide Bond

Peptides are the products formed by the condensation of two or more amino acids through their amino and carboxylic groups involving elimination of water molecules. They may be classified as *dipeptides, tripeptides* and *polypeptides* depending upon whether the number of amino acid molecules taking part in condensation is *two, three* or *more than three* respectively. *The linkage (—CO—NH—) which unites various amino acid units in a peptide molecule* is called **peptide** linkage or **peptide bond.**

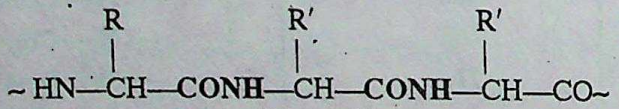


A simple convention is used to write the structure and name of the peptide. The amino acid unit having free —NH_2 group is called **N-terminal end** whereas the amino acid unit with free —COOH group is called **C-terminal end.** The structure is written with *N-terminal end to the left* and *C-terminal end to the right.* The base name of the peptide is taken from the C-terminal amino acid unit. Other amino acid units are taken to be substituents of this acid and the suffix *ine* of their name is replaced with *yl.* In case of polypeptides and proteins the abbreviated names of amino acid units are used. Let us write the structure of a tripeptide formed from *glycine, alanine* and *serine*



Glycylalanylserine (*Name*) Gly-Ala-Ser (*Abbreviated name*)

A section of polypeptide with different amino acid units is given below :



Polypeptide

16.3. PROTEINS

Proteins are the complex organic substances which are the basis of protoplasm and are found in all living organisms. The name protein (Greek, *proteios* means *first*) was introduced by Mudlar (1839) because of prime importance of such substances to animal life.

In general, proteins are polymers of α-amino acids. Like peptides the amino acid units in proteins are held up by peptide (—CONH—) linkage. In fact, a polymeric products of α-amino acid with molecular mass upto 10000 are called *polypeptide* while those having molecular mass more than 10000 are considered as *proteins.*

Classification of Proteins

A. Classification based upon molecular structure

Proteins can be classified into two broad classes on the basis of their molecular structure : ***Fibrous proteins*** **and** ***Globular proteins.***

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(*i*) **Fibrous proteins.** Such proteins have thread like molecules which tend to lie side by side to form fibres. The molecules are held together at many points by hydrogen bonds. They are generally insoluble in water.

Functions of fibrous proteins. Fibrous proteins serve as the chief structural material of animal tissues. For example, *keratin*, in skin, hair, nails, wool, horn and feathers : *collagen* in tendons, *myosin* in muscle, *fibroin* in silk.

(*ii*) **Globular proteins.** Such proteins have molecules which are folded into compact units that often approach spheroidal shapes. The areas of contact between the molecules are small. Therefore, the inter-molecular forces, here, are comparatively weak. These proteins are soluble in water or aqueous solutions of acids, bases or salts.

Functions of globular proteins. Globular proteins perform diversity of biological functions. Some of these are :

(*a*) *Some globular proteins function as enzymes* which catalyse all biological reactions. Insulin and thyroglobin are some examples.

(*b*) *Some globular proteins regulate metabolic processes.* For example, the protein hormone *insulin* (from pancreas) maintains blood-sugar level.

(*c*) *Some globular proteins act as antibodies which* protect the body from the effect of invading species and thus, save *us from diseases.*

Some **important differences** between *globular proteins* and *fibrous proteins* are given below in tabular form :

Globular proteins	*Fibrous proteins*
1. They are cross-linked condensation polymers of acidic and basic amino acids.	1. They are linear condensation products.
2. They are soluble in water or aqueous solutions of acid bases or salts.	2. They are insoluble in common solvents but soluble strong acidic or basic solutions.
3. They are folded to give rise in three dimensional spheroidal shape.	3. The long linear protein chains are held together by intermolecular H-bonds.
4. Examples : *Albumins* in egg, *Enzymes* and some *hormones* etc.	4. Examples ; *Fibroin* in silk ; *collagen* in tendons ; *myosin* in muscles. etc.

B. Classification based upon the corresponding hydrolysis products. On the basis of chemical composition or the nature of products of hydrolysis, proteins are classified into three categories.

(*i*) **Simple proteins.** *These proteins on hydrolysis give mixture of α-amino acids only.* Some examples are *albumins* in white of egg, *oxyzenin* in rice, *Keratin* in hair, nails, horns and *glutenin* in wheat.

(*ii*) **Conjugated proteins.** *These proteins on hydrolysis give a non-protein part in addition to the α-amino acids. This non-protein portion is called the prosthetic group.* The main function of the prosthetic group is to control the biological functions of the protein. Some examples of conjugate proteins along with their corresponding prosthetic groups are given below in tabular form

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Name of the protein	*Prosthetic group*
Nucleoproteins	Nucleic acids
Glycoproteins or Mucroproteins	Sugars
Lipoproteins	Lipids such as lecithin
Phosphoproteins	Phosphoric acid residues
Chromoproteins (Haemoglobin and Myoglobin)	Some colouring matter such as red coloured protoporhyrin (Heme)

(*iii*) **Derived proteins.** *These are the degradation products obtained by partial hydrolysis of simple or conjugated proteins with acids, alkalies or enzymes.* Some examples are, proteoses, peptones and polypeptides.

Proteins ⟶ Proteoses ⟶ Peptones ⟶ Polypeptides

Structure of proteins

The structure of proteins is generally discussed under three headings as described below :

1. Primary Structure of Proteins

Primary structure *of proteins refers to the sequence in which amino acids are arranged in proteins.* Each protein has a specific sequence of amino acid units which is critical of its biological activity. The change of just one amino acid in the sequence can alter the biological activity. For example, *haemoglobin* a protein responsible for carrying oxygen in the blood consists of 574 amino acid units. The change of just one amino acid in the sequence produces ineffective haemoglobin (which is found in the patients suffering from sickle cell anaemia).

—Val—His—Leu—Thr—Pro—**Glu**—Glu—Lys—

(*Normal haemoglobin*)

—Val—His—Leu—Thr—Pro—**Val**—Glu—Lys

(*Sickle cell haemoglobin*)

The procedure for the determination of primary structure of protein is quite complex. Such procedure was first of all developed by *Frederic Sanger* in 1953, who determined the amino acid sequence in *insulin* shown in Fig. 16.1.

Insulin has 51 amino acids arranged in two polypeptide chains which are cross-linked at two places by disulphide linkage one chain has 21 amino acids while the other chain has *13 amino acids.*

The principal source of insulin for medicinal use has been the pancreas of cattle. Now-a-days, synthetic insulin is also available. The synthesis of insulin has become possible by the method of genetic engineering.

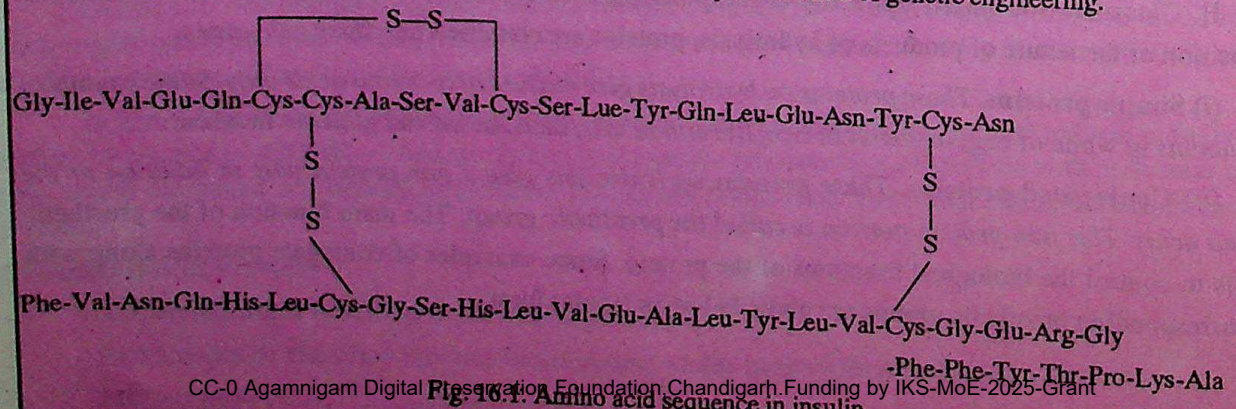

Fig. 16.1. Amino acid sequence in insulin.

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2. Secondary Structure of Proteins

Secondary structure *of the proteins refers to the arrangement of polypeptide chains which arises as a result of hydrogen-bonding.* The two common type of secondary structures are discussed as follows :

(*a*) **Pleated sheet structure or β-sheet structure.** In this type of secondary structure, the peptide chains lie side by side in a *zig-zag* manner with alternate R-groups on the same side. The neighbouring peptide chains are held together by intermolecular H-bond resulting in the formation of flat shut type structure. These sheets are stacked one above the other like the folded pages of the book to form three dimensional structure called the β-pleated (folded) sheet structure shown in Fig. 16.2 (*a*) and (*b*) the silk protein fibroin has β-pleated sheet structures.

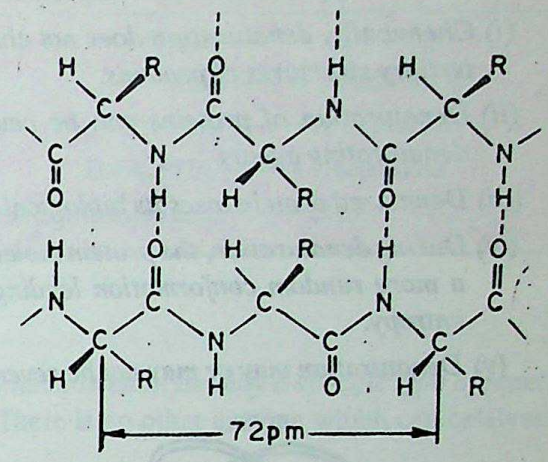

Fig. 16.2. Pleated sheet structure.

(*b*) **α-Helix structure.** In this type of structure, the peptide chains are coiled up to form a **helix** (like spiral staircase or a cork screw). The helical pattern is found to be right-handed and is called *α-helix*. The H-bonds (*intramolecular*) are formed between C = O group of one amino acid residue and N—H group of fourth amino acid residue. The α-helix and H-bonding in α-helix has been shown in Fig. 16.3. Proteins such as *myosin* in nucleus and *keratin* in hair, wool, nails the have α-helix structures.

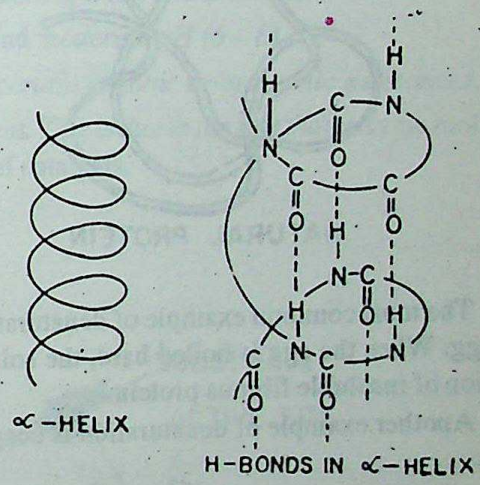

Fig. 16.3

It may be noted that ***pleated sheet type structure*** *generally exists in case if R-groups are smaller whereas* ***α-helix type structure*** *is assumed if R-groups are larger.*

3. Tertiary Structure of Proteins

Tertiary structure *of proteins refers to the definite geometric pattern in which the entire protein molecule folds up to produce a specific shape.* It arises due to folding and superposition of various secondary structural elements. The two important tertiary structures of proteins are *fibrous structure* and *globular structure*. It may be noted that the relative stability of the tertiary structure depends upon the interactions between various parts of the protein molecules through the substituents present in the side chains of constituents amino acids. These interactions may be any of the following :

ionic or salt bridge
hydrogen bonds
van der Waal's interaction or
disulphide (S—S) bonds.

Denaturation of Proteins

Proteins are very sensitive to the action of heat, mineral acids, alkalies, etc. On heating or treatment with mineral acids, soluble forms of proteins such as globular proteins often undergo coagulation or precipitation to give fibrous proteins which are insoluble in water. This coagulation also results in the loss of the biological activity of the protein. That is why, *the coagulated proteins so formed are called* **denatured proteins.**

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The process that brings about changes in physical as well as biological properties of the proteins is called denaturation of proteins. Some important features of denaturation are

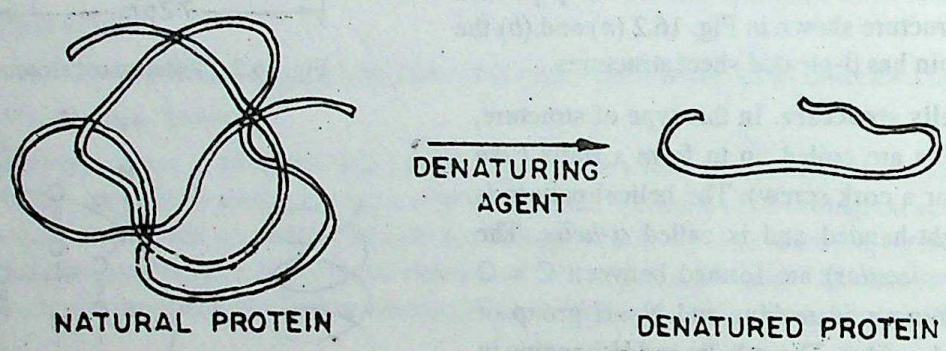
(*i*) *Chemically, denaturation does not change the primary structure but changes the secondary and tertiary structures of proteins.*

(*ii*) *Denaturation of proteins can be caused by changes in pH, temperature or by adding other denaturating agents.*

(*iii*) *Denatured protein loses its biological activity.*

(*iv*) *During denaturation, the protein molecule uncoils from an ordered and specific conformation into a more random conformation leading to precipitation. Thus denaturation leads to increase in entropy.*

(*v*) *Denaturation may or may not be reversible.*



The most common example of denaturation of proteins is coagulation of albumin present in white part of an egg. When the egg is boiled hard, the soluble globular protein present in it is denature resulting in the formation of insoluble fibrous protein.

Another example of denaturation is coagulation of milk in the presence of lemon juice (*acid*) to form *cheese*.

16.4. ENZYMES

Enzymes *are the important group of globular proteins which act as biological catalysts in living systems.* Without enzymes, the living process will be too slow to sustain life. For example, without enzymes in our digestive tract it would take us about 50 years to digest a single meal. In the similar way, the hydrolysis of a peptide in laboratory requires very drastic conditions, like prolonged heating with a base but in living systems the hydrolysis of proteins occurs very rapidly in the presence of enzymes. About 3000 different kinds of enzymes have been identified so far. Some common enzymes alongwith their functions have been given in Table 16.2.

Table 16.2. Some Common Enzymes

Enzymes	*Reaction catalysed*
Amylase	Starch $\longrightarrow$ Glucose
Maltases	Maltose $\longrightarrow$ Glucose
Lactase	Lactose $\longrightarrow$ Glucose + Galactose
Invertase	Sucrose $\longrightarrow$ Glucose + Fructose
Urease	Urea $\longrightarrow$ $CO_2 + NH_3$

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Enzymes	*Reaction catalysed*
Carbonic anhydrase	$H_2CO_3 \longrightarrow CO_2 + H_2O$
Pepsin	Proteins $\longrightarrow$ Amino acids
Trypsin	Proteins $\longrightarrow$ Amino acids
Nucleases	DNA, RNA $\longrightarrow$ Nucleotides
DNA Polymerase	Deoxynucleotide triphosphates $\longrightarrow$ DNA

Characteristics of Enzymes

Some common characteristics of enzymes are :

1. *They are highly specific in their action. Each enzymes can catalyse only a specific type of reaction.* For example, *maltase* catalyses the hydrolysis of maltose. There is no other enzyme which can catalyse the hydrolysis of maltose.

2. *They can speed up an uncatalysed reaction to the extent of a ten million times.*

3. *The are active at moderate temperature* (≈ 310 K) and *moderate pH (6 – 8).*

4. *Their action can be controlled or even inhibited by certain organic or inorganic substances.*

5. *Even a small amounts of enzymes can be highly efficient. This is due to the fact that* enzyme molecules are regenerated during their catalytic activity just like chemical catalysts.

Coenzymes

Certain enzymes require non-proteinous components for their activity. These components could be *metal ions* like Zn^{2+}, Mg^{2+}, Mn^{2+}, Cn^{2+}, Co^{2+}, K^+, Na^+, etc., or small *organic molecules* and are collectively called **co-enzymes.** Many of the co-enzymes for biological processes are derived from vitamins like *thiamine, niacin, riboflavin,* etc. In such enzymes the protein part of the enzyme is called the **apoenzyme.** Neither coenzyme nor apoenzyme can alone catalyse the reaction. The two must combine before they can act as a catalyst.

Mechanism of Enzyme Activity

The stepwise mechanism of enzyme catalysed reaction as proposed by Michaeli and Menten (1913) is being described as follows.

The reactant molecule (usually called **substrate**) binds itself to the *active site* on the surface of enzyme. The active site in given enzyme is so shaped that only a specific substrate can fit in it, just as a lock can be opened only with a specific key. The specific binding results in the formation of **enzyme-substrate complex** (Fig. 16.4). Also referred to as *activated complex.*

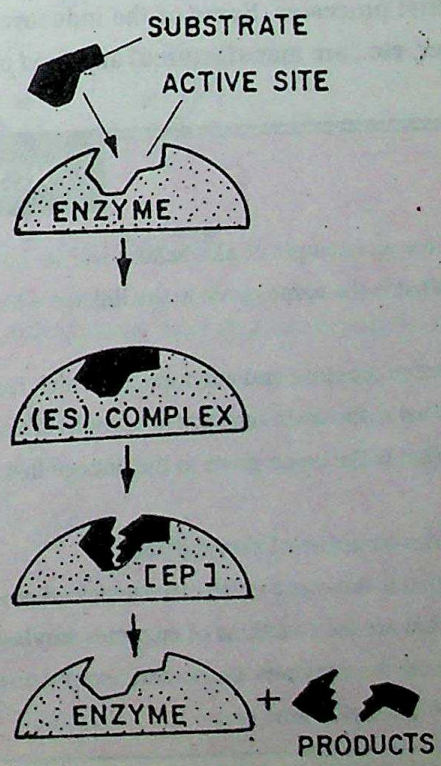

Fig. 16.4. Activity of Enzymes.

In the complex, the substrate is placed in the proper orientation to facilitate the chemical reaction

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and enhancing its rate. The complex finally decomposes to give products and regenerated enzymes. The general reaction scheme can be represented as :

Step I. *Binding of substrate* (S) *to enzyme*

$$E + S \longrightarrow \underset{\text{Complex}}{[ES]}$$

Step II. *Product formation of the complex*

$$[ES] \longrightarrow EP$$

Step III. *Release of the product from the enzyme*

$$EP \longrightarrow \underset{\text{Enzyme}}{E} + \underset{\text{Product}}{P}$$

Applications of Enzymes

(*i*) **Prevention of diseases.** The deficiency of enzymes in living system can cause certain diseases. For example, *phenyl ketone urea*—a congenital disease in children is caused by deficiency of the enzyme *phenyl alanine hydroxylase. Similarly, albinism* is another disease which is caused by the deficiency of an enzyme *triosinase.* Such diseases can be *prevented* by the supply of enzymes through diet.

(*ii*) **Curing of diseases.** Enzymes are also used to treat diseases related to heart. For example, an enzyme *streptokinase* is used to dissolve blood clots.

(*iii*) **Industrial applications.** Besides biological reactions, enzymes also find tremendous applications in industrial processes. Some of the industries which bank upon the use of enzymes are : *breweries* (where wine, beer, etc., are manufactured) and *food processing industries.*

REVIEW QUESTIONS

16.1. Give an example of aldohexose and an aldotriose. **Ans.** *Glucose-Aldohexose-Glyceraldehyde-Aldotriose.*

16.2. What is the name given to the linkage which holds together two monosaccharides units in a polysaccharide ? **Ans.** *Glycoside linkage*

16.3. Out of amylose and amylopectin which form of starch is soluble in water ?

16.4. What is the main function of carbohydrates in the living bodies ?

16.5. What is the name given to the linkage that holds together the amino acid molecules in proteins ? **Ans.** *Peptide linkage.*

16.6. Draw structure of alanylglycine.

16.7. What is the cause of disease sickle cell anaemia ?

16.8. What are the functions of enzymes amylase and trypsin ?

16.9. Name the enzymes whose deficiency causes the following diseases.

(*i*) Phenyl ketone urea (*iii*) Albinism.

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16.5. NUCLEIC ACIDS

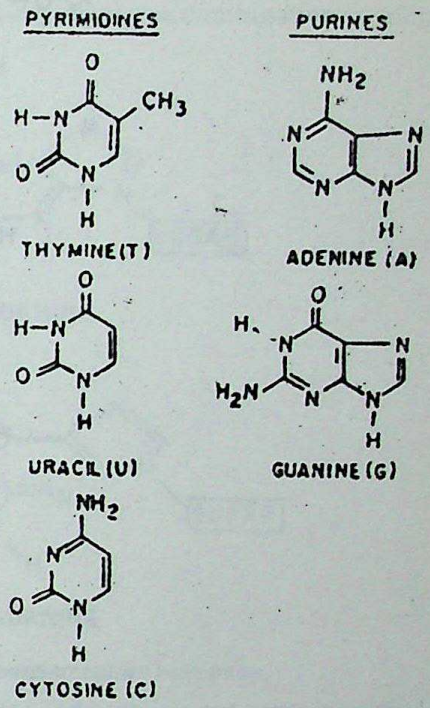
Nucleic acids are long chain polymers that are present in high concentration in the nuclei of cells. They play vital role in the cell replication and protein synthesis. Nucleic acids are of two types :

(*i*) DNA (*Deoxyribonucleic acid*)
(*ii*) RNA (*Ribonucleic acid*).

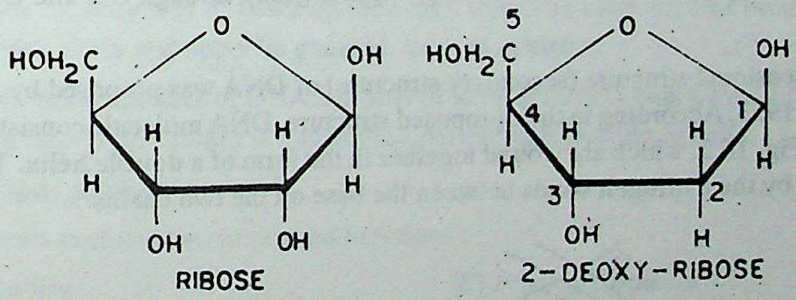
The monomeric units of nucleic acids are called nucleotides. Each nucleotide consists of three parts : *a phosphate group, a five carbon sugar* and *a nitrogen containing heterocyclic base.* The nitrogen containing bases found in nucleotides are derivatives of either *purine* or *pyrimidine.*

The bases derived from purine are *adenine (A)* and *guanine (G)* whereas those derived from pyrimidine are *thymine (T), uracil (U)* and *cytosine (C).* The base thymine is found only in nucleotides of DNA and the base uracil is found only in nucleotides of RNA.

The second component of the nucleotides is the sugar molecule. The sugar present in RNA is D-ribose and in DNA is D-2-deoxyribose.

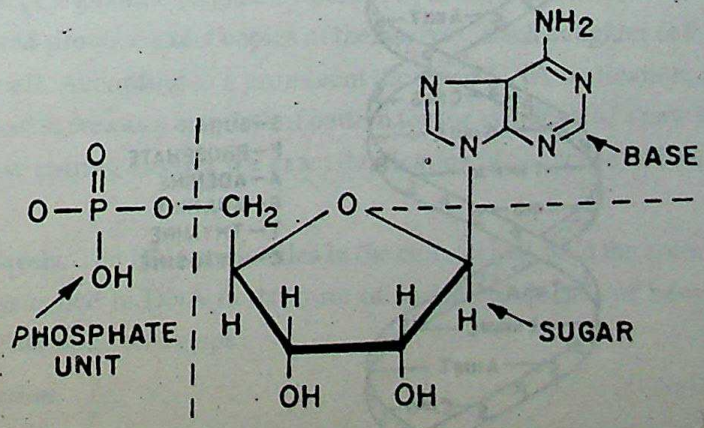


Bases in nucleic acids.



Sugars in nucleic acids.

The bonding between sugar molecule, phosphoric acid and nitrogenous base in a nucleotide is shown as follows :



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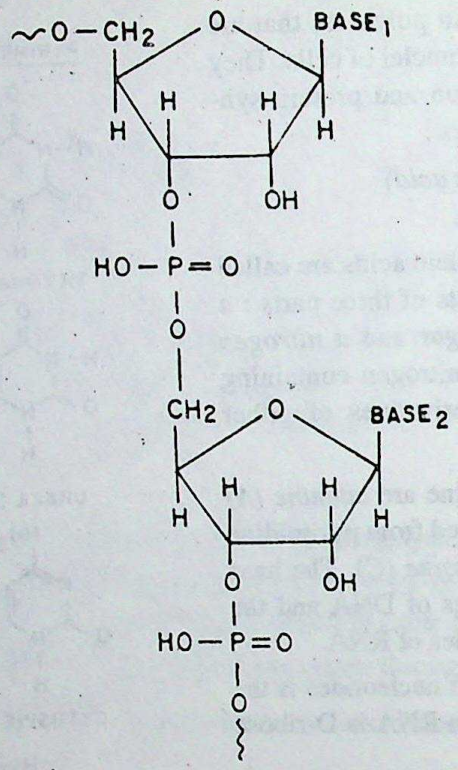
In nucleic acids, the nucleotides are linked to form long chains as shown below :



In nucleic acids sugar portions are joined to phosphate group through C-3 and C-5 hydroxyl groups.

Structure of DNA

The three dimensional structure (secondary structure) of DNA was proposed by Jame D. Watson and Francis H.C. Crick in 1953. According to their proposed structure, DNA molecule consist of two linear strands of the type shown in Fig. 16.5, which are wound together in the form of a **double helix.** The two chains of the double helix are held by the hydrogen bonds between the base on the two chains.

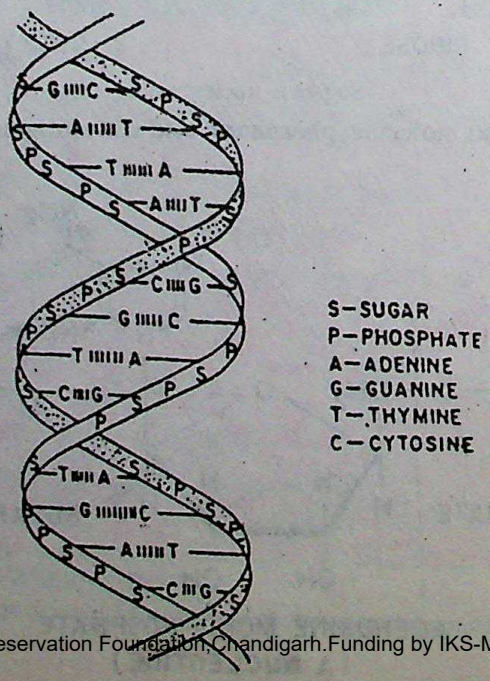


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Fig. 16.5. Double helix structure of DNA.

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The hydrogen bonding between bases of the two strands is highly specific. Thymine (T) pairs with adenine (A) through two hydrogen bonds and cytosine (C) pairs with guanine (G) through three hydrogen bonds (Fig. 16.6). Corresponding to the structure of these bases, the above combination is energetically most

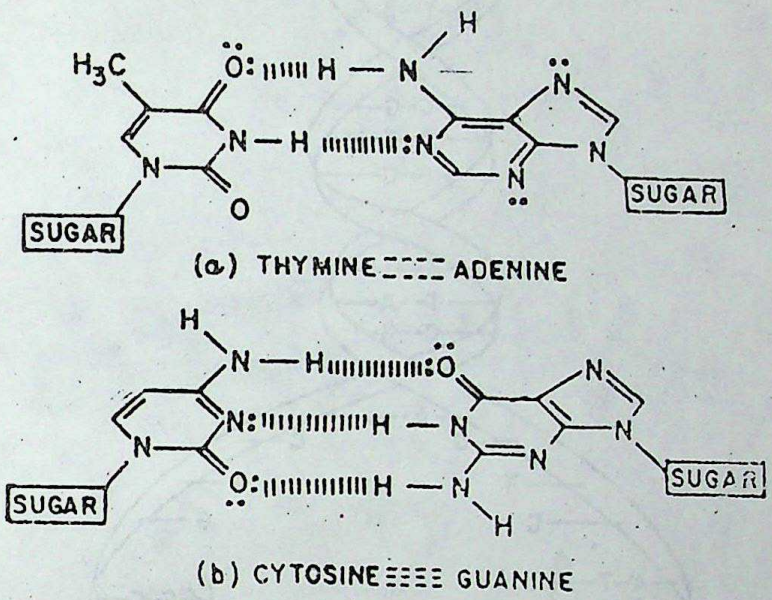

Fig. 16.6. Hydrogen bonding between complementary base pairs.

favoured. The other combinations are energetically less favoured and hence do not occur in normal DNA. This means that the two strands of DNA are **complementary** to each other. The sequence of bases on one strands automatically fixes the sequence of bases on the other. Opposite each adenine on one chain there is always a thymine on the other chain and opposite guanine, there is cytosine.

The double helix structure of DNA has proved to be helpful in understanding protein synthesis and the means by which genetic information is transmitted during reproduction of cells.

Functions of Nucleic Acids

Nucleic acids perform two important functions :

(*a*) *Replication* (*b*) *Protein synthesis.*

Replication. *It is the property of biomolecule to synthesise exact copy of itself.* DNA has this unique property of duplicating itself. The genetic information for the cell is coded in the form of the sequence of bases adenine (A), thymine (T), guanine (G) and cytosine (C) in the DNA molecules. During division of cell, DNA molecules replicate and produce exact copies of themselves. Each daughter cell has DNA molecules identical to that of the parent cell. According to a prominent theory of DNA replication, the two strands of DNA helix unwind and each strand serves as a template of pattern for the synthesis of a new strand in the cell environment. The specificity of base pairing ensures the exact duplication of sequence of bases in the reproduced strand of DNA (Fig. 16.7).

Protein synthesis. The DNA molecules in the cell nucleus hold the code for the protein synthesis. The genetic information is coded in DNA in the form of specific sequence of bases. The synthesis of a specific protein involves the following two steps :

(*i*) *Transcription*

(*ii*) *Translation*

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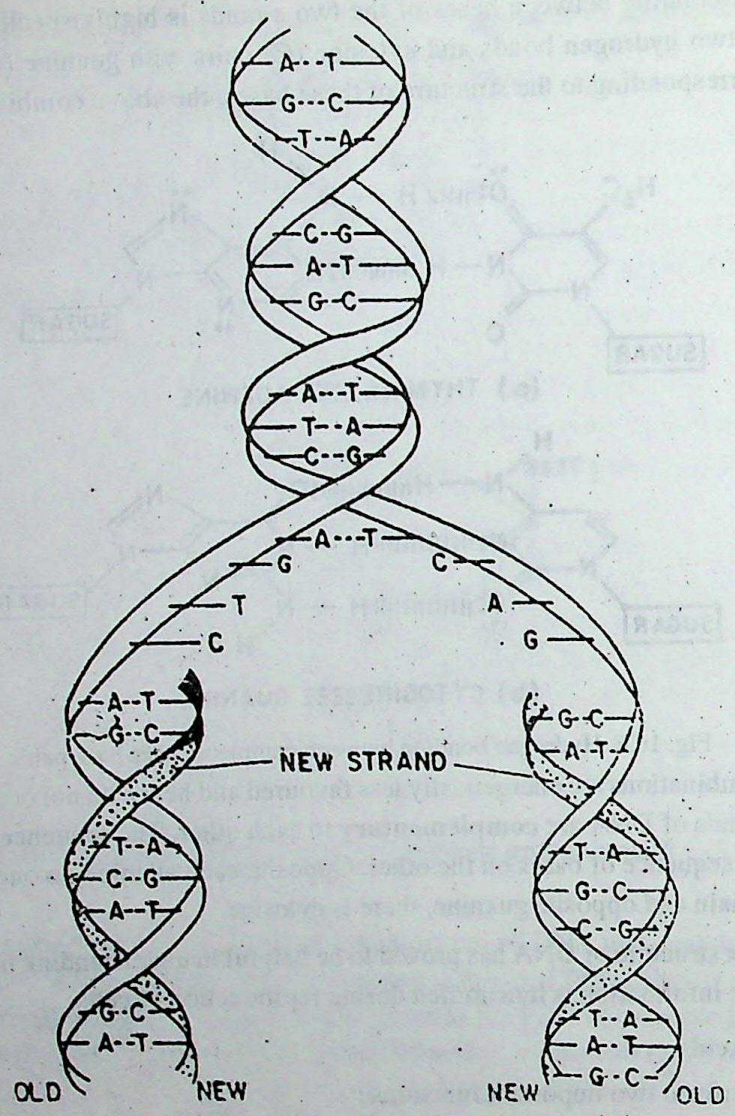

Fig. 16.7. Replication of DNA molecule.

The **transcription** *involves copying of sequence of bases from the DNA strand on the RNA molecule called messenger RNA (mRNA).* The bases of the mRNA are complementary to those of the DNA strand. Messenger RNA contains only four bases adenine (A), guanine (G), cytosine (C) and uracil (U). DNA molecules contain the four bases adenine (A), guanine (G), cytosine (C) and thymine (T). The complementary base pairs are as follows :

DNA	*mRNA*
Adenine (A)	Uracil (U)
Guanine (G)	Cytosine (C)
Cytosine (C)	Guanine (G)
Thymine (T)	Adenine (A)

After transcription mRNA moves from the nucleus of the cell to a ribosome in the cytoplasm where it serves as template for the protein synthesis (Fig. 16.8).

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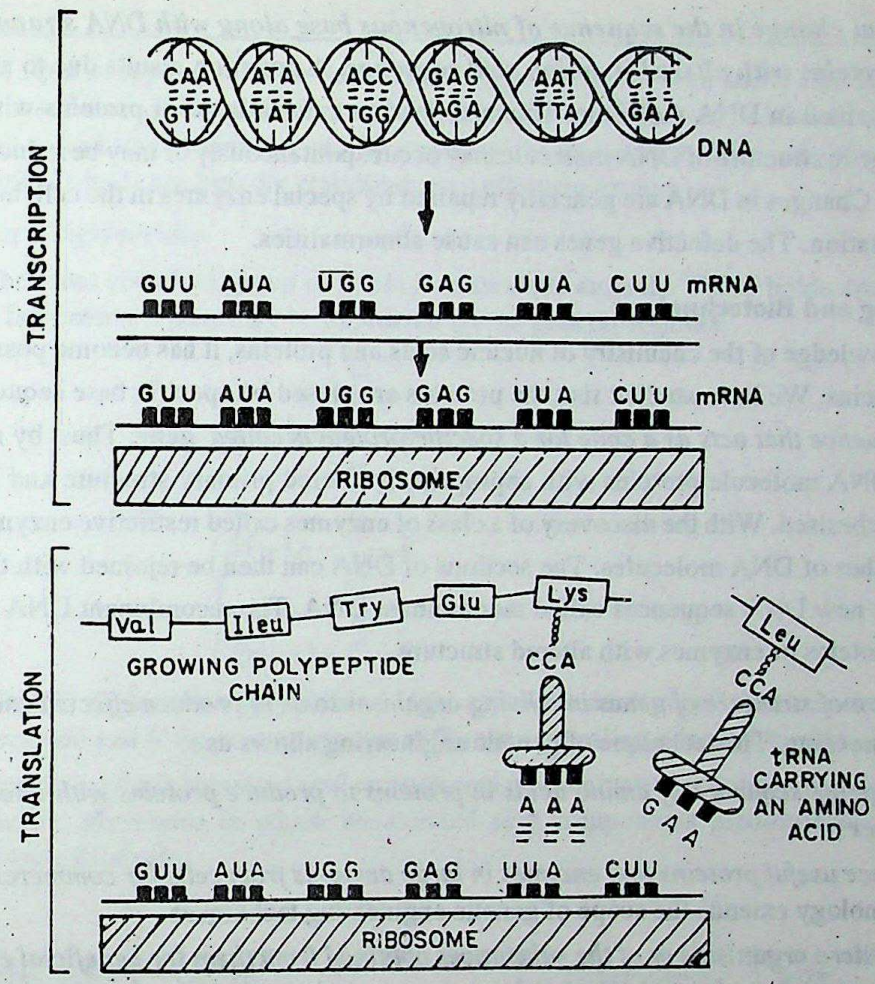

Fig. 16.8. Role of DNA and RNA in protein synthesis.

The sequence of bases in mRNA are read in a serial order in groups of three at a time. Each triplet of nucleotides (having a specific sequence of bases) is known as **codon**. Each codon specifies one amino acid. Many amino acids have more than one codons. The amino acids are brought to the mRNA by another type of RNA and called **transfer RNA (tRNA)**. Each amino acid has at least one corresponding tRNA. At one end of the tRNA molecule is a trinucleotide base sequence that is complementary to some trinucleotide base sequence on mRNA. The other end of tRNA molecule carries a specific base sequence of three nucleotides —CCA— with a —OH group on the sugar exposed on the terminal adenine nucleotide.

This —OH group combines with a specific amino acid and carries it to the mRNA. The complex between mRNA and tRNA is stabilized by another type of RNA called **ribosome RNA (rRNA)**. After transfer of amino acid, the tRNA is free to go back and repeat the process. Thus, proteins with a specific sequence of amino acids are produced. The sequence of amino acids in proteins is determined by the sequence of nucleotide bases on mRNA which in turn is determined by the sequence of bases in DNA molecule. *The DNA sequence that acts as a code for a specific protein is called* **gene.** Every protein in the cell has a corresponding gene. *The relationship between the nucleotide triplets and the amino acids is called* **genetic code.**

Synthesis of proteins in the body takes place at very fast rate. Only minutes after the radioactive amino acids are injected into the animals, radioactive proteins can be found.

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Mutations

It is a chemical change in the sequence of nitrogenous base along with DNA strands that can lead to the synthesis of proteins with altered α amino acid sequence. A mutation results due to an alternation of the genetic code contained in DNA molecule. This may lead to the synthesis of proteins with a new amino acid sequence. Change in structure of DNA molecule may occur spontaneously or may be induced by radiation, chemical agents, etc. Changes in DNA are generally repaired by special enzymes in the cell, however, failures to do so result in mutation. The defective genes can cause abnormalities.

Genetic Engineering and Biotechnology

From the knowledge of the chemistry of nucleic acids and proteins, it has become possible to regulate the synthesis of proteins. We have studied that the proteins are closed by specific base sequences in nucleic acids. *The DNA sequence that acts as a code for a specific protein is called* **gene.** Thus, by manipulation of base sequences in DNA molecule proteins with appropriately altered primary structure and hence modified functions can be synthesised. With the discovery of a class of enzymes called restrictive enzymes it is possible to cut specific stretches of DNA molecules. The sections of DNA can then be rejoined with the help of other enzymes to produce new DNA sequences called recombinant DNA. The recombinant DNA is then used for the production of proteins or enzymes with altered structure.

The alteration of structure of genes in a living organism so as to produce effects beneficial to man is called **genetic engineering.** The technique of genetic engineering allows us :

(*i*) *to change the sequence of amino acids in proteins to produce proteins with altered and desired properties* ;

(*ii*) *to produce useful proteins and enzymes in large amounts from cells for commercial applications.* Biotechnology extends the scope of genetic engineering techniques.

***The use of micro organisms or of the substances obtained from them for beneficial effect in industry or in other processes is referred to as* biotechnology.**

Although the fields of genetic engineering and biotechnology are in the early stages of development yet they have made significant contributions in the field of human health and medicine, agriculture and industry.

(*i*) Genetic engineering has made possible the early diagonosis and treatment of many genetic disorders.

(*ii*) Many biotechnology products are used as medicines. Some of these are listed below :

(*a*) *Human insulin hormone* which is used for the treatment of diabetes.

(*b*) *Interferon,* an anti-viral agent.

(*c*) *Blood clotting factor VIII,* used for the treatment of haemophilias.

(*d*) *Vaccines* for various diseases such as typhoid, cholera, measles, tetanus, etc.

(*iii*) In petrochemicals, micro-organisms developed for growth on oil and hydrocarbons, help in recovery of valuable raw materials and also act as environmental depollutants:

(*iv*) In food and chemical industry also, the micro-organisms can be genetically engineered to carry out specific steps.

(*v*) In the field of agriculture, with the help of genetic engineering it is possible to develop certain varieties of crops which are resistant to diseases.

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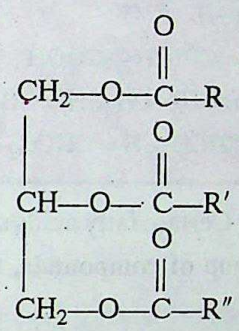
16.6. LIPIDS

The term lipid is applied to *those constituents of plant and animal tissue that are insoluble in water but are soluble in solvents of low polarity, such as chloroform, carbon tetrachloride, ether or benzene.* For lipid, we cannot assign any definition on the structural basis because different types of compounds are considered as lipids. Lipids are broadly classified into following groups :

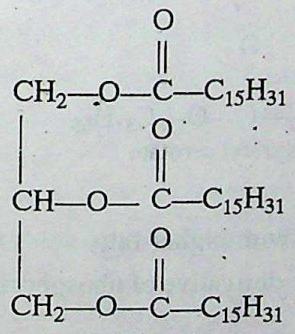
Simple Lipids or Triglycerides

This is the most abundant group of lipids in plants and animals. These lipids are triesters of glycerol with long chain fatty acids. These may be expressed by the general formula

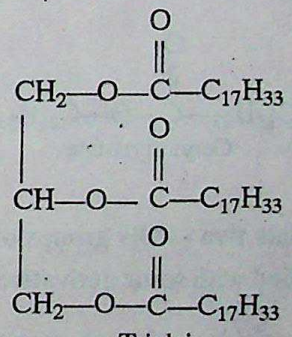


These triesters are known as **glycerides.** If the glyceride contains all the three same acid groups, it is called *simple glyceride* and if the acid groups are different, it is called *mixed glyceride.*

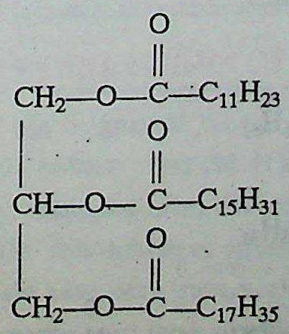
The glyceride in which saturated acid components predominate, are solid at room temperature and are called **fats** while the glycerides in which unsaturated acid components predominate, are liquid at room temperature and are called **oils.**



Tripalmitin
(A simple glyceride)



Triolein
(A simple glyceride)



Glyceryl lauropalmito-stearate
(A mixed glyceride)

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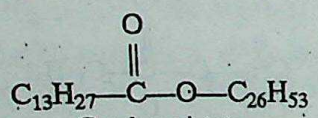
Oils can be converted into fats by hydrogenation. Hydrolysis of glycerides yields glycerol and fatty acids. The naturally occurring fatty acids have an even number of carbon atoms. Some of the fatty acids generally present in glycerides are listed below :

Fatty Acid	*Structure*
Lauric acid	$CH_3(CH_2)_{10}COOH$
Myrstic acid	$CH_3(CH_2)_{12}COOH$
Palmitic acid	$CH_3(CH_2)_{14}COOH$
Stearic acid	$CH_3(CH_2)_{16}COOH$
Oleic acid	$CH_3(CH_2)_7CH = CH(CH_2)_7COOH$
Linoleic acid	$CH_3(CH_2)_4CH = CH—CH_2CH = CH(CH_2)_7COOH$
Linolenic acid	$CH_3CH_2CH = CHCH_2CH = CHCH_2—CH = CHCH_2COOH$

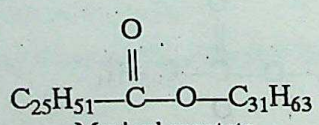
Fatty acids are major source of energy in the cell. Certain fatty acids such as linoleic acid and linolenic acid permit the body to synthesize a very important group of compounds, the prostaglindins which control almost all the physiologic activity of the body.

Waxes

These lipids are esters of higher fatty acids with long chain monohydric alcohols. These are solids having melting points between 310—373 K. For example, bees wax is largely ceryl myristate. *Carnauba wax* is mainly myricyl cerotate. It is obtained from Brazilian palm tree. Waxes are used in cosmetics, shoe polish, candles and ointments.



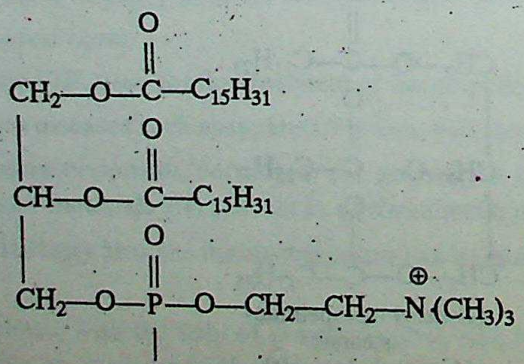
Ceryl myristate



Myricyl cerotate

Phospholipids

In phospholipids two —OH groups of glycerol are esterified with higher fatty acids while the third —OH group is esterified with some derivative of phosphoric acid. The derivative of phosphoric acid contains an alcoholic compound that may be choline. $[HOCH_2CH_2\overset{+}{N}(CH_3)_3]OH$, ethanolamine ($HOCH_2CH_2NH_2$) or serine ($HOCH_2CHNH_2CO_2H$). For example, lecithin



Lecithin

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Phospholipids form structures of cell membranes especially in nerve cells. Phospholipids have a polar water attracting phosphate group and a non-polar water repelling group of two fatty acid chains. This presence of polar and a non-polar group in the same molecule makes phospholipids good emulsifiers and provides them with membrane forming properties.

Cellular Membranes

The major constituents of cell membranes are *phospholipids* and *cholines*. The relative ratio of these constituents is different in different cells. The phospholipids are arranged in a double layer, with their polar ends projecting outside and non-polar ends into the interior of the membrane. This allows the polar phosphate ester groups to interact with aqueous surroundings both inside as well as outside the cell. The non-polar ends remain away from the aqueous medium. The protein components of the membrane are either embedded in the double layer of phospholipids or are attached to sides of the membrane. Cell membranes possess many specific **functions** in living bodies. Some of the important functions of cell membranes are :

(*i*) *They maintain the shape of the cell.*

(*ii*) *They protect the cells from injury and mechanical shock.*

(*iii*) *They keep the cell contents in place.*

(*iv*) *They regulate the flow of materials into and out of the cell i.e., they selectively keep out certain compounds and transport others.*

(*v*) *They allow cell to cell recognition and contain receptors for many enzymes, hormones etc.*

REVIEW QUESTIONS

16.10. Name the four bases present in RNA molecule.

16.11. Name the sugar portion present in the nucleotides of DNA molecule.

16.12. Name the base that pairs with adenine in RNA molecule. What is the corresponding base present in DNA molecule ?

16.13. What are the two main functions of nucleic acids ?

16.14. Name the three different types of RNA.

16.15. What is the formula of choline ? **Ans.** $[HOCH_2CH_2\overset{+}{N}(CH_3)_3]\overset{-}{OH}$

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16.7. CHEMICAL EVOLUTION AND ORIGIN OF LIFE

Where, when and how life originated on the Earth ? According to geologists, astronomers and biologists, the Earth is about 5000 million years old. It is believed that at that time it was a violent place with a high level of volcanic activity, torrential rains and continuous earth-quacks of all magnitudes due to the contraction of cooling surface. The atmosphere of primitive earth must also have been totally different. Since the temperature of the crust would have been quite high, all the water must have been present as vapours in the atmosphere. The volcanic activity must have produced large quantities of H_2, CH_4, CO_2 and NH_3 along with some other gases. We can arrive at this conclusion by the study of volcanic activity taking place presently. Under these violent conditions the oxygen and ozone must be absent from the atmosphere in free state. In the

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absence of ozone shield, the Earth must be exposed to harsh ultraviolet and other smaller wavelength radiations. As the Earth cooled the water vapours must have condensed and collected in the form of small pools on the Earth.

Under the violent conditions prevailing on the primitive Earth, it is believed that the gases reacted to from small organic molecules. The best evidence in favour of this comes from the experiments started by Stanley Miller in the U.S.A. Attempts were made to simulate the conditions that are thought to have existed on the primitive Earth. It was observed that when electric discharge (simulated lightning), is passed, through a mixture of gases such as CO_2, CH_4, NH_3 and H_2 in the presence of water vapours, small quantities of a variety of organic compounds is produced (Fig. 16.9). Many of these compounds such as amino acids were of great biological importance. Mixtures of amino acids heated on powdered rock and quenched by cooling (simulated rain) have resulted into polypeptides whose structures are similar to those of naturally occurring proteins. The synthetic nucleic acids have also been shown to possess self-replicating properties similar to their natural counter-parts.

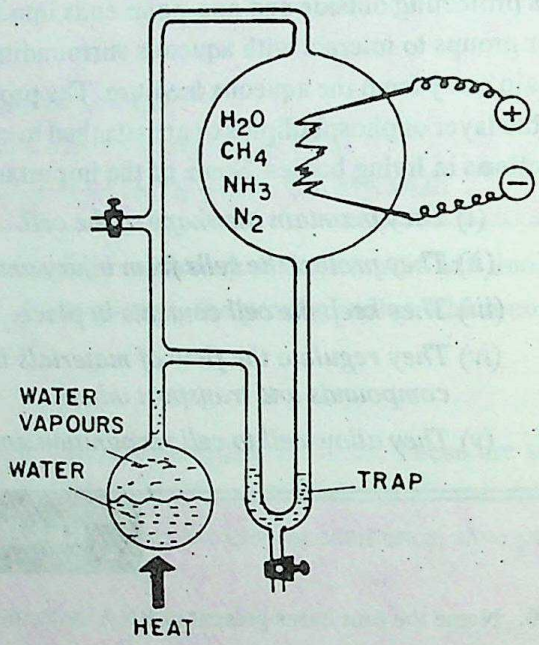

Fig. 16.9

It is thus reasonable to believe that the above type of reactions must have taken place in the Earth's early stages. The slow condensation and accumulation of water on the surface of the Earth would have served as solvent for these compounds. Thus, there would have been numerous ponds and lakes of dilute organic '*soup*'. The process of evolution must have started with the formation of polypeptides and self-replicating polynucleotides and nucleic acids under the effect of violent condition prevailing on the primitive Earth. When phospholipid molecules combined to form membranous structure sealing a mixture of proteins and polynucleotides, the first cell was born. This probably happened 3.5 to 4 billion years ago.

Now let us consider how the changes took place that brought about change in the Earth's atmosphere and transformed it into oxygen-rich gas mixture. The first oxygen was definitely produced by photodissociation of water vapours. Hydrogen must also have been formed, but this would have escaped quickly from the Earth's atmosphere. In the beginning oxygen would also have been rapidly consumed in oxidizing the material of the Earth's crust, but as these became fully oxidized, the level of free oxygen in the atmosphere would have increased. However, according to Dr. Harold Urey the oxygen level could not have risen beyond 2% as a result of photodissociation. This is due to the reason that as free oxygen accumulates it tends to shield the Earth from the ultra-violet radiations. Amount of ozone also would have increased in the atmosphere. This is also a particularly good absorber of UV radiation. As the ultraviolet radiation was cut out by the accumulation of oxygen and ozone in the atmosphere, the polymerization of the self-replicating unit in the cells would have taken place and the organic units could grow much bigger. The building up of the oxygen concentration in the atmosphere must have taken place slowly as a result of activity of autotrophic organisms over the millions of the years. Oxygen is the byproduct of photosynthesis. The increase in the proportion of oxygen in atmosphere permitted the development of aerobically respiring heterotrophs.

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SOME IMPORTANT TERMS

- **Biomolecules.** The complex organic molecules which built up living organism and form the basis of life.
- **Biochemistry.** The branch of chemistry which deals with study of chemical composition and structure of living organism and chemical changes taking place in them.
- **Carbohydrates.** The polyhydroxy aldehydes or ketones or the compounds which can produce then on hydrolysis.
- **Glycoside linkage.** The linkage which connects the monosaccharide units in oligosaccharides or polysaccharides.
- **Mutarotation.** The process involving the gradual change in the optical rotation of either optically active form of carbohydrate in aqueous solutions to that of equilibrium mixture.
- **Annomers.** The pair of diastereomers of aldoses which differ in configuration about C_1 carbon atom.
- **α-Amino acids.** The organic compounds containing COOH group and an amino group at the α-carbon atom. These are the building blocks of proteins and peptides.
- **Proteins.** The complex nitrogenous organic molecules which are essential for the growth and maintenance of life.
- **Enzymes.** The biological catalyst produced by living cells which catalyst the biochemical reactions in living organism. All enzymes are globular proteins.
- **Nucleic acids.** The biologically important polymers present in the living cells which play significant role in synthesis of proteins in living organism and are responsible for the transfer of genetic information.
- **Replication.** It is a unique property of the biomolecule such as DNA to synthesise an exact copy of itself.
- **Gene.** The DNA sequence that codes for a specific protein or polypeptide is called a gene.
- **Genetic code.** It is the relationship between the nucleotide triplet amino acid sequence.
- **Mutation.** It is a chemical change in a DNA molecule that could lead to the synthesis of proteins with different amino acid sequence.
- **Lipids.** These are oily, fatty or waxy substances present in the living organism which constitute those structural components of plants and tissues which are soluble in organic solvents and are sparingly soluble in water. They are energy reservoir of the cell.

EXERCISES

VERY SHORT ANSWER QUESTIONS
(1 Mark)

1. Give one example of phospholipid.
2. What type of enzymes can cause the hydrolysis of starch ? *[A.I. CBSE (O) 1992]*
3. What type of bonding occurs in globular proteins ? *[CBSE (1) 1992]*
4. What type of bonding occurs in α-helix configuration ?
5. What is the name given to the relation between the nucleotide triplet and amino acids ?
6. What is genetic engineering ?

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7. Name the enzyme which is used to cure the heart diseases.
8. Name the polysaccharide which represents the polymeric structure of β-D-glucose units.
9. Name the two important functions of carbohydrates in the living bodies.
10. What do the following abbreviations represent : *ala, val, leu, gly* ?
11. What is peptide bond ?
12. What is a nucleotide ? *(A.I. CBSE 1993)*
13. What will be the sequence of bases on *m*-RNA molecule synthesised on the following strand of DNA

    TATCTACCTGGA ?
14. What is invert sugar ?
15. What is a nucleoside ?
16. What is Zwitter ion ? Give Zwitter ion structure of glycine and glycylalanine.
17. What is gene ? *(Har. Board 1994)*
18. What is genetic code ? *(Har. Board 1994)*
19. Name the linkage holding amino acids in a polypeptide.
20. The deficiency of which enzyme causes albinism ?
21. What is the sequence of bases on *m*RNA molecule synthesized on following strand of DNA

    TATCGACGA. *(CBSE Board 1995)*
22. Select Vitamins and Hormons from the following :

    (*i*) Maltose (*ii*) Insulin (*iii*) Riboflavin
    (*iv*) Thiamine (*v*) Adrenalin (*vi*) Glucose
    (*vii*) Cellulose (*viii*) Estrone. *(Har. Board 1995)*
23. Write the sequence of basis on *m*RNA molecule synthesised on the following strand of DNA

    AGCGATTAC *(CBSE 1995)*
24. Define mutation. *(CBSE 1997)*

DESCRIPTIVE QUESTIONS
(2 Marks)

25. Give the open chain and ring structure of D-Glucose.
26. What are carbohydrates ? How are they classified ? Give examples.
27. What are polysaccharides ? Give one example. *[CBSE (4) 1992]*
28. Explain the formation α and β anomers of glucose.
29. Give the structure of

    (*i*) Sucrose (*ii*) α-D-fructose (*iii*) Maltose.
30. Describe the structure of amylose, amylopectin and cellulose.
31. (*a*) Describe the functions of carbohydrates in living organism.

    (*b*) What is mutarotation ?
32. What are proteins ? State a difference between

    (*a*) A fibrous protein and a globular protein

    (*b*) α-helix and β-pleated sheet structure of protein.

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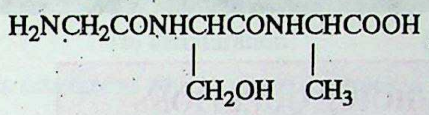
33. What are amino acids ? How do they constitute peptides ? Give the abbreviated name of the following tripeptide :



34. What do you understand by primary, secondary and tertiary structures of proteins ?
35. What is meant by denaturation of proteins ? *(CBSE 1994 S)*
36. What are enzymes ? Give some important examples. Give important applications of enzymes.
37. What is the biological importance of proteins ? *(CBSE 1993 S)*
38. What are proteins ? How are they formed ? What is their primary structure ? *(CBSE Board 1992)*
39. Describe the mechanism of activity of enzymes.
40. Certain diseases are caused by enzyme deficiencies. Explain giving a specific example. *(CBSE 1992)*
41. Describe the secondary (double helix) structure of DNA.
42. What are the main functions of DNA ?
43. What are nucleic acids ? Mention their two important functions. *(CBSE 1992)*
44. Explain the functions of nucleic acids in protein synthesis. *(CBSE 1992)*
45. Define the following terms :
    (*i*) Gene (*ii*) Codon (*iii*) Genetic code.
46. Explain, how proteins are synthesized in living bodies ?
47. What are lipids ? What are their main types ?
48. What are phsopholipids ? What is their significance in living organisms ? *[A.I. CBSE 1993 ; CBSE (1) 1992]*
49. What is the difference between oils and fats ? How can we convert oils into fats ?
50. What are the main functions of lipids ?
51. What are the functions of nucleic acid ?
52. What are triglycerides and phsopholipids ?
53. How are proteins, peptides and α-aminoacids related ?
54. Discuss the structure and functions of cell membranes.
55. Distinguish between
    (*i*) a globular protein and fibrous protein (*ii*) α-Glucose and β-Glucose
    (*iii*) primary structure and secondary structure of protein. *(CBSE 1994)*
56. Name the three nucleic acids which are used in protein synthesis.
57. Name the scientists who :
    (*i*) gave three dimensional structure of DNA
    (*ii*) was awarded nobel prize for synthesis of insulin.
58. What is the source of pectin ? What is its use ? *(H.P. Board 1993 S)*
59. What is meant by colloidon ?
60. Describe briefly the following : *(CBSE 1997)*
    (*i*) Transcription (*ii*) Translation

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select the correct answer from following questions :

1. What of the following is an example of aldohexose ?
   (*a*) Ribose (*b*) Fructose (*c*) Sucrose (*d*) Glucose.
2. The linkage which holds various amino acid units in primary structure of proteins is
   (*a*) glycoside linkage (*b*) peptide linkage (*c*) ionic linkage (*d*) hydrogen bond.
3. Maltose is made of
   (*a*) α-D-glucose (*b*) α and β-D-glucose (*c*) Glucose and fructose (*d*) Fructose only.
4. The amino acids are the end products of the digestion of
   (*a*) lipids (*b*) fats (*c*) proteins (*d*) enzymes.
5. Fructose has
   (*a*) bitter taste (*b*) sweet taste (*c*) tasteless (*d*) nothing certain.
6. The constituent units of sucrose are
   (*a*) lactose and glucose (*b*) glucose and fructose (*c*) galactose and glucose (*d*) glucose and maltose.
7. When hemiacetal reacts with alcohol, the product is
   (*a*) dihemiacetal (*b*) alcohol (*c*) peptide (*d*) acetal.
8. Amylopectin is a polymer of
   (*a*) β-D-glucose (*b*) α-D-glucose (*c*) β-D-fructose (*d*) α-D-fructose.
9. α-helix refers to
   (*a*) primary structure of proteins (*b*) secondary structure of proteins
   (*c*) tertiary structure of proteins (*d*) quaternary structure of proteins.
10. Which of the following bases is not present in DNA ?
    (*a*) Adenine (*b*) Gaunine (*c*) Uracil (*d*) Cytosine.
11. The relation between nucleotide triplets and the amino acids is called
    (*a*) Transcription (*b*) Duplication (*c*) Genetic code (*d*) Gene.
12. Nucleic acids are polymers of
    (*a*) nucleotides (*b*) nucleosides (*c*) nuclei of heavy metals (*d*) proteins.
13. The latter D in carbohydrates signifies
    (*a*) dextro rotatory (*b*) mode of synthesis (*c*) its configuration (*d*) its diamagnetic nature.
14. Which disaccharide is present in milk ?
    (*a*) maltose (*b*) galactose (*c*) sucrose (*d*) lactose.
15. Glucose and fructose are
    (*a*) isomers of each other (*b*) homologues of each other
    (*c*) annomers of each other (*d*) enantiomers of each other.
16. Invert sugar is
    (*a*) a variety of cane sugar (*b*) optically inactive form of sugar

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(*c*) mixture of glucose and fructose in equimolar proportion

(*d*) mixture of glucose and galactose.

17. The destruction of the biological nature and activity of proteins by heat or chemical agent is called

(*a*) dehydration (*b*) denaturation (*c*) denitrogenation (*d*) deammination.

18. The non-proteinous substances which certain enzymes require for their activity are called

(*a*) Catalysts (*b*) Inhibitors (*c*) Co-enzymes (*d*) Epimers.

19. Which of the following is an ester ?

(*a*) Kerosene oil (*b*) Soap (*c*) Bees wax (*d*) Peptoeses.

20. Which of following is not a glyceride ?

(*a*) Lipids (*b*) Fats (*c*) Phospholipids (*d*) Soaps.

FILL IN THE BLANKS

Fill in the blanks with proper items :

1. Insulin is secreted by .....
2. The three parts of a nucleotide are : a phosphate group, a base and a .....
3. The linkage holding monosaccharide units in maltose is .....
4. Primary structure of proteins refers to .....
5. The sugar in RNA is .....
6. The helical structure of proteins is stabilised by .....
7. The three dimensional structure of DNA was proposed by .....
8. All enzymes are .....
9. The chemical changes in DNA molecule that could lead to synthesis of proteins with an altered amino acid sequence is called .....
10. ..... is a monosaccharide which is sweeter than sucrose.

TRUE/FALSE STATEMENTS

Mark the following statements true or false :

1. The enzyme resin is used for the co-agulation of milk.
2. Lecithin is an example of β-amino acid.
3. Amylopectin is a branched chain polymer of α-D glucose.
4. Pyranose ring structure contains five carbons and one oxygen atom.
5. The property of a biomolecule to synthesise exact copy of itself is called transcription.
6. The amino acid units in a polypeptide are linked by peptide bond.
7. The three dimensional structure of DNA was proposed by Watson and Crick.
8. The sugar unit in DNA is D-Ribose.
9. All the carbohydrate can be represented by the formula $C_x(H_2O)_y$.
10. The enzymes which convert urea to CO_2 and NH_3 are called urease.
11. A defective haemoglobin causes sickel cell anaemia.

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12. Cheese is an example of denatured protein.

MATCHING TYPE QUESTIONS

Match the items given in column A with that given in Column B :

Column A	Column B
1. Phospholipids	1. Linkage in carbohydrates
2. Nucleotide	2. Linkage in proteins
3. Peptide linkage	3. A sugar and heterocyclic base combination
4. Glycoside linkage	4. Major constituent of cell membranes
5. Nucleoside	5. The monomeric unit in nucleic acids

HINTS AND ANSWERS

VERY SHORT ANSWER QUESTIONS

1. Lecithin **2.** Amylase

6. It is the process of alteration of structure of genes in living organism so as to produce effect beneficial to man.

7. Streptokinase **8.** Cellulose

9. The act as *constituents of cell membrane* and also as *biofuels.*

10. *alanine, valine, lucine, glycine.*

11. The bond which links various amino acid units in peptides and proteins (—CO—NH—).

13. AUAGAUGGACCU

14. Equimolar mixture of α-D glucose and β-D fructose

15. Product formed by attachment of a nitrogenous base (purine or primidine) to the sugar unit (ribose or deoxyribose) at C_1 by β-linkage.

16. $\overset{+}{N}H_3—CH_2—COO^-$ (glycine) ; $\overset{+}{N}H_2—CH_2—CO—NH—\underset{}{\overset{CH_3}{\overset{|}{CH}}}—\overset{-}{COO}$ (glycylalanine)

19. Peptide bond **20.** Tyrosinase **21.** AUAGCUGCT

22. Hormones are : Insulin, Adrenalin, Estrone ; Vitamines are : Riboflavin, Thiamine

23. UCGCUAAUG

DESCRIPTIVE QUESTIONS

55. *m*RNA, *t*RNA and *r*RNA **56.** (*i*) Watson and Crick (*ii*) Frederic Sanger

57. Fruit skin ; for making Jellies **58.** It is a solution of proxylin in ether and alcohol.

MULTIPLE CHOICE QUESTIONS

1. (*d*)	**2.** (*b*)	**3.** (*a*)	**4.** (*c*)	**5.** (*b*)	**6.** (*b*)
7. (*d*)	**8.** (*b*)	**9.** (*b*)	**10.** (*c*)	**11.** (*c*)	**12.** (*a*)
13. (*c*)	**14.** (*d*)	**15.** (*a*)	**16.** (*c*)	**17.** (*b*)	**18.** (*c*)
19. (*c*)	**20.** (*d*).				

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FILL IN THE BLANKS

1. pancreas
2. a sugar
3. glycoside linkage
4. sequence of α-amino acids
5. D-ribose
6. H-Bonds
7. James Watson and Francis Crick
8. globular proteins
9. mutation
10. Fructose.

TRUE/FALSE STATEMENTS

1. True
2. False
3. True
4. True
5. False
6. True
7. True
8. False
9. False
10. True
11. True
12. True.

MATCHING TYPE QUESTIONS

1—4, 2—5, 3—2, 4—1, 5—3.

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17

Chemistry of Some Biological Processes

LEARNING OBJECTIVES

In this unit, we shall learn about

- *Carbohydrates and their metabolism ;*
- *Blood, haemoglobin and respiration ;*
- *Immune system ;*
- *Vitamins and hormones ;*
- *Simple idea of chemical evolution.*

In unit 16, we learnt about the structure of some biomolecules. In this unit, we shall study the function of some important biomolecules in the living organism. A living system is a complex array of chemical reactions. The contents of living cells are in a dynamic state *i.e.*, the complex molecules are constantly synthesised, and degraded after performing their functions. The healthy living cell is characterised by a **"steady state conditions"** in which the rates of build up and breakdown are nearly the same. *The set of chemical reactions which lead to the synthesis of complex organic molecules* constitute **anabolism** whereas *the series of reactions which involve the breakdown of complex organic molecules* in the living systems refer to **catabolism.** Synthesis and degradation collectively constitute **metabolism.** Let us study some biological processes in brief.

17.1. CELLULAR ENERGETICS

Energetics of chemical processes occurring in biological systems are not the same as those in non-biological systems. We have already learnt in thermodynamics that only those chemical processes are favourable and spontaneous which proceed with a decrease of free energy ($\Delta G < 0$). In a cell many chemical reactions do occur with a negative sign of ΔG. The common example being the stepwise degradation of sugar to carbon dioxide and water. However, the cells also involve several chemical reactions with $\Delta G > 0$, although they are energetically unfavourable from the thermodynamics point of view. Synthesis of macromolecules during anabolism is a common example of this type.

In may be noted that biochemical processes in which $\Delta G > 0$ are called **endergonic reactions** whereas those in which $\Delta G < 0$ are called **exergonic reactions.** In order to understand as to how endergonic reactions occur in biological systems, let us assume two hypothetical reactions as described below :

(*i*) $X \longrightarrow Y$; $\Delta G_1 > 0$ (*Energetically unfavourable*)

(*ii*) $A \longrightarrow B$; $\Delta G_2 < 0$ (*Energetically favourable*).

The reaction (*i*) is energetically not favourable. But if such a reaction is *coupled with* reaction (*ii*) which is energetically favourable, then the energy involved during reaction (*ii*) will be used up in reaction (*i*), thus, making it spontaneous. Thus, the net free energy change in two processes is negative.

$$\Delta G_{total} = (\Delta G_1 + \Delta G_2) < 0$$

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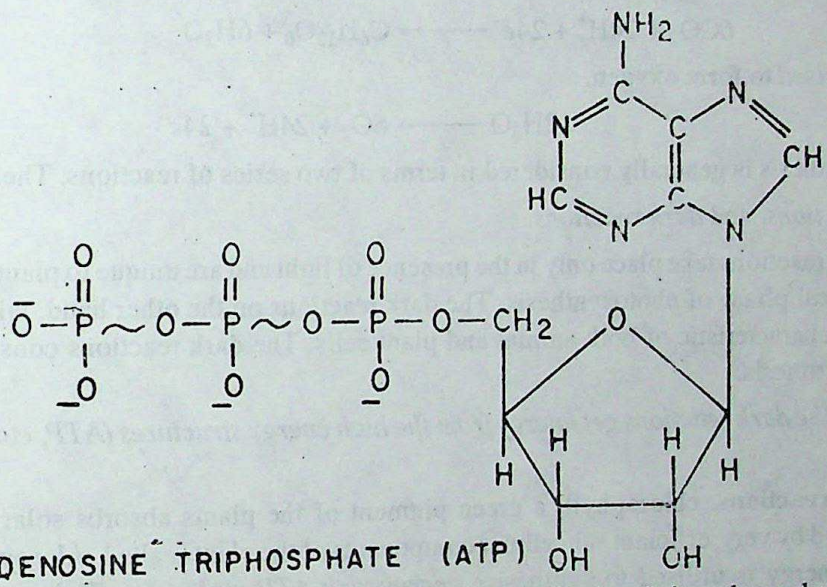
In the similar way, the energy consuming steps ($\Delta G > 0$) in biological processes are accomplished by coupling these to energy releasing ($\Delta G < 0$) reactions in such a way so that the net free energy change in the two steps is negative. All energy requiring cellular reactions occur by this principle of coupling. In most of the cellular processes, the energy producing reaction is the *hydrolysis of adenosine triphosphate* (ATP). Let us study as to why adenosine triphosphate is an energy rich molecule.

ANDENOSINE TRIPHOSPHATE (ATP)

The structure of *adenosine triphosphate* has been shown below :



ADENOSINE TRIPHOSPHATE (ATP)

ATP molecule contains two *high energy phosphate bonds*. The bonds have been shown in the structure by a wiggle (~) line. It may be noted that these bonds are not different from the conventional chemical bonds. In fact, the rich energy content of ATP molecule is due to the four highly electronegative oxygen atoms around each phosphorus. The repulsive forces among these cause the increase in the energy content. During hydrolysis of ATP molecule, the repulsive forces between oxygen atoms are reduced and there is a release of large amount of free energy. The release of free energy for hydrolytic reactions of ATP have been shown below :

Adenosine triphosphate (ATP)

↓ (Hydrolysis)
Energy released = 30.93 kJ mol^{-1}

Adenosine diphosphate (ADP)

↓ (Hydrolysis)
Energy released = 28.42 kJ mol^{-1}

Adenosine monophosphate (AMP)

Such energy producing hydrolytic reactions are coupled to energy needing reactions in the cell. Besides this, such reactions also provide energy to the cell for performing different kinds to work like *contraction of muscles, uptake of nutrients, movement of the cell, transmitting nerve impulses* etc. Thus, ATP can be considered as the pivot of various activities of the cell.

Let us now study the principal ways by which cells obtain energy for the synthesis of ATP. These are *photosynthesis* and *catabolism of nutrients* like carbohydrates are lipids.

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17.2. PHOTOSYNTHESIS

Sun is the ultimate source of energy that is required in metabolism. The enormous amount of energy is radiated into space by the sun. The solar energy is taken up by the plants and is used up to produce organic molecules like carbohydrates and amino acids. ***The process of synthesis of energy rich carbohydrates from carbon dioxide and water in the presence of sunlight is called photosynthesis.*** In its simplified form the reaction can be written as

$$6CO_2 + 6H_2O + \textit{Solar energy} \longrightarrow C_6H_{12}O_6 + 6O_2$$

It may be noted that in photosynthesis, carbon dioxide is *reduced* to form sugar,

$$6CO_2 + 24H^+ + 24e^- \longrightarrow C_6H_{12}O_6 + 6H_2O$$

and water is *oxidised* to form oxygen.

$$12H_2O \longrightarrow 6O_2 + 24H^+ + 24e^-$$

Photosynthesis is generally considered in terms of two series of reactions. These are :

light reactions, and *dark reactions.*

The light reactions take place only in the presence of light and are unique to plants only. They constitute the **photochemical phase** of photosynthesis. The dark reactions on the other hand, take place in the absence of light and are characteristic of both animal and plant cells. The dark reactions constitute the **biosynthesis** phase of photosynthesis.

In short, *the dark reactions get energy from the high energy structures (ATP, etc.) produced during the light reactions.*

In **light reactions,** chlorophyll, a green pigment of the plants absorbs solar energy which is subsequently grabbed by very efficient subcellular components of the plants called *chloroplasts* through the series of steps. This energy is utilised to synthesise *energy-rich ATP molecules.* The water molecules undergo photolysis and are oxidised to molecular oxygen, O_2.

Thus, in light reactions, *the solar energy is ultimately transferred to the universal storehouse or biochemical energy, in the form of adensosine triphosphate (ATP).*

In **dark reactions,** conversion of atmospheric carbon dioxide into glucose and other carbohydrates takes place through series of steps. The energy needed for this process is supplied by the ATP molecules. It may be noted that for the synthesis of one molecule of glucose 18 molecules of ATP are used up. The overall process can be represented as

$$\textit{Carbon dioxide} + \textit{Water} + \textit{Solar energy} \xrightarrow[\textit{Steps}]{\textit{Series of}} \textit{ATP} + O_2 + \textit{Organic molecules}$$

$$6CO_2 + 6H_2O \xrightarrow{18\ ATP} \underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2$$

REVIEW QUESTIONS

17.1. Which molecule can be considered as the pivot of various activities of the cell ?

17.2. Which series of reactions involving photosynthesis pertain to plants only ?

17.3. Which series of reactions involving photosynthesis constitute biosynthesis phase ?

17.4. How may molecules of ATP are used for the synthesis of 1 molecule of glucose during photosynthesis ?

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17.3. DIGESTION

We have learnt that plants can synthesise organic molecules like carbohydrates, fats, etc., of their own from inorganic substances like carbon dioxide and water. However, animals do not possess this ability. Therefore, they depend directly or indirectly on plants for such substances. They consume them in the form their food. The food materials ingested by the organism is generally not suitable as such for cellular consumption. The food must undergo degradation in order to carry on metabolic activities. ***The process of conversion of undiffusable form of food into diffusable or simpler form with the help of enzymes*** is called **digestion.** In mammals, the enzymatic digestion occurs mainly in *mouth, stomach* and *small intestine.* In this section, we shall learn about the digestion of carbohydrates, lipids and proteins.

Carbohydrate Digestion

The principal form of carbohydrates in our food are :

polymers like starch and glycogens,

disaccharides like sucrose and lactose, and

simple sugars like glucose and fructose.

The digestion of carbohydrates starts in the mouth by the action of enzymes *amylase* or *ptyalin* present in the saliva. The enzymes bring about the hydrolysis of starch and glycogens to maltose to a limited extent. In the stomach, the digestion of carbohydrates stops because the enzyme ptyalin is rendered inactive due to high acidity of gastric juices in the stomach. As the food passes from stomach into intestine, it gets mixed up with *enzymes* secreted by pancreas. These enzymes hydrolyse polysaccharides to maltose and maltose to glucose. At the same time they catalyse other hydrolytic reactions. The final result is a mixture of simple sugars such as glucose, fructose, galactose, etc. which are absorbed into blood stream and ultimately pass into liver. The enzymes present in the liver convert galactose into glucose. It may be noted that a number of polysaccharides like cellulose, which do form the part of our diet are not nourishing because there are no enzymes to digest them. However, cellulosic fibre ingested with diet helps in normal functioning of large intestine.

Glucose absorbed into blood is the major source of energy for cells. Cells of brain and nervous system depend entirely on blood glucose for their function. The concentration of blood sugar is regulated by the hormone *insulin.* If sugar level is *too high,* simple sugars are converted into polysaccharide and glycogens in the liver. On the other hand, if the blood sugar level is *too low,* the stored glycogen gets hydrolysed to raise the level. Malfunctions of our biological system can lead to *too much blood sugar* (called **hyperglycemia**) or too low blood sugar (called **hypoglycemia**). Either of these conditions indicates one or the other type of diabetes.

Digestion of Lipids

Lipids denote a group of compounds which includes fats and oils (unit 16). The digestion of fats and oil occur primarily in *intestinal tract* (*small intestine*). Here, the food gets mixed up with *bile fluids* or *bile salts* secreted by the liver. Bile fluids emulsify the fats or oils whereas the enzyme *lipases* bring about the hydrolysis of fats into glycerol and fatty acids, which subsequently passes into bloodstream.

Protein Digestion

The digestion of proteins begins in the stomach and continues in the small intestine. The enzymes of protein digestion are :

(*i*) **proteases,** which help in the breakdown of large protein molecules into peptides, and

(*ii*) **peptidases,** which covert peptides into amino acids.

The acidic environment in stomach causes denaturation of proteins prior to digestion. The breakdown of dietary proteins that begins in stomach with pepsin continues in the intestine in the presence of trypsin, chymotrypsin and various other peptidases secreted by pancreas and intestine. The amino acid formed as result

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of protein breakdown are absorbed into bloodsteam through intestinal mucosa. These amino acids may reassemble to form new proteins or may undergo further breakdown.

17.4. METABOLISM

Metabolism refers to all chemical reactions necessary for the foodstuff to be utilised by the body. It includes both physical as well as chemical aspects of life processes. In general, the chemical reactions or changes which are concerned with the production of heat to maintain body temperature and to supply energy for the vital activities constitute **energy metabolism.** The living systems produce energy either in the presence of oxygen or in the absence of oxygen. Systems which produce energy in the absence of oxygen are **anaerobic** whereas those which require oxygen for the production of energy are said to be **aerobic.**

The series of chemical reactions which produce energy by breaking down the complex organic molecules into smaller one constitute **catabolism.** On the other hand, the synthesis of various complex cell molecules constitutes **anabolism.** Both anabolism and catabolism depend on one another and in the absence of one, the other does not exist. Both **catabolism** and **anabolism** take place at extremely rapid rate in the presence of specific enzymes and they collectively constitute **metabolism.**

Carbohydrate Metabolism

Time and again we have pointed out that glucose is the primary source of cellular energy. In cells, glucose is gradually oxidised in large number of steps to carbon dioxide and water. During *catabolism* of glucose, energy is released. This energy is utilised for the synthesis of ATP. During degradation of glucose, many intermediate molecules are formed which act as starting points for *anabolic synthesis* of amino acids.

The oxidation of glucose can be divided into two stages as described below :

1. First stage. The first stage of oxidation does not require oxygen and is anaerobic process. It is called **glycolysis.** Glycolysis occurs through series of successive steps in which glucose breaks down to pyruvic acid. The stepwise sequence through which degradation occurs is often called **Embden-Meyerhof pathway.** Glycolysis occurs in *cytoplasm of the cell* and it is the means by which anaerobic cells produce ATP.

In many micro-organisms and plants, where there is a limited oxygen supply also, the pyruvic acid gets converted into ethyl alcohol and CO_2. It may be noted that under anaerobic condition there occurs a net gain of 2ATP molecules for each molecule of glucose breaking down to pyruvic acid.

2. Second stage. The second stage of glucose oxidation requires oxygen and is *aerobic.* It is referred to as *cellular respiration.* It involves the conversion of pyruvic acid (formed in the first stage) into carbon dioxide and water through a series of steps. The process occurs in *mitochondria of the cells.* The pyruvic acid oxidises to from CO_2 and *acetyl coenzyme A.* The acetyl coenzyme A further enters into series of cyclic reactions, which is called **citric acid cycle or Kreb's cycle.** The acetyl coenzyme A formed from pyruvic acid

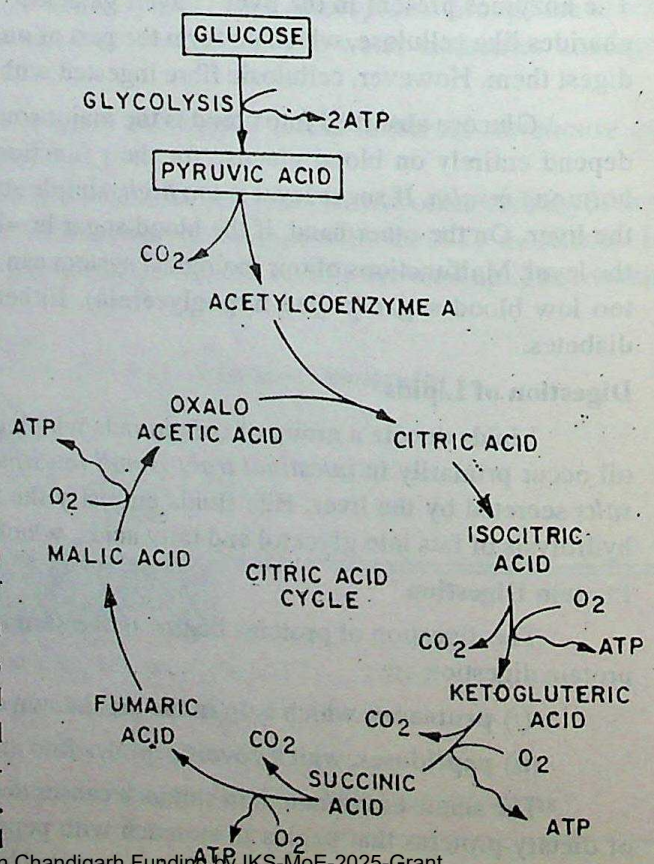

Fig. 17.1. First and second stage of glucose metabolism.

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condenses with oxalo-acetic acid to initiate the series of cyclic transformations. The oxalo-acetic acid is regenerated in the last step of the citric acid cycle and cause the commencement of a new citric acid cycle. *Citric acid cycle in fact, forms the central pathway for the final oxidation of carbohydrates, fats* and most of the *amino acids*. The first and second stages of glucose metabolism in brief have been shown in Fig 17.1.

Electron transfer chain. At several steps during the oxidation of glucose, both during glycolysis as well as the Kreb's cycle, the electrons and hydrogen atoms are removed by certain co-enzymes whereas at other steps these are accepted. These series of oxidation reduction reactions constitute *electron transfer chain* and it results in the formation of most of the ATP molecules.

Energy relationship in carbohydrate metabolism. In many organisms the anabolic reactions acquire energy from catabolic reactions. The fundamental agents responsible for these energy exchanges are ATP and ADP. The energy released in exergonic reactions is stored by conversion of ADP to ATP.

The exact way in which ADP and ATP enter into metabolic processes is beyond the scope of the book. It may be noted that the metabolic conversion of 1 mole of glucose to CO_2 and H_2O is accompanied by the conversion of 38 moles of ADP to ATP

$$C_6H_{12}O_6 + 6O_2 + 38ADP + \underset{\text{Inorganic phosphate}}{38Pi} \longrightarrow 6CO_2 + 6H_2O + 38ATP$$

Assuming that 31 kJ of energy is absorbed for conversion of one mole of ADP into ATP we find that about 1178 kJ of energy is stored from the metabolism of 1 mole of glucose because 1 mol of glucose converts 38 mol of ADP to ATP. The total amount of energy released when 1 mole of glucose is converted into CO_2 and H_2O is $\approx 41\%$. This is certainly greater than any device humans have designed for energy utilisation. The rest of energy is liberated as heat and is used to maintain the body temperature.

Lipid Metabolism

In the lipids (fats), most of the energy is contained in the long hydrocarbon chains of fatty acids. These are the main *energy reserves* of the body. They produce about 375 kJ of energy per gram on oxidation, which is much more than that generated by oxidation of carbohydrates or proteins (≈ 16 kJ mg^{-1}). The fatty acids are oxidized in *mitochondria of liver cells* and *skeletal muscles*. During this process, the acetyl coenzyme A is generated first which enters the citric acid cycle for the production of ATP as described earlier. For example, palmitic acid, a C – 16 fatty acid produces 130 molecules of ATP.

$$\textit{Lipids} \xrightarrow{\textit{hydrolysis}} \textit{Fatty acids} + \textit{Glycerol} \xrightarrow{\textit{oxidation}} \textit{Acetyl Co A} \xrightarrow[\textit{cycle}]{\textit{citric acid}} \textit{ATP}$$

Protein Metabolism

It has been pointed out earlier in the digestion of proteins that amino acids are absorbed into blood from intestine. They are the dietary source of nitrogen in the body. These are used in the *formation of new cells* or *repairing of old cells* or *synthesis of other amino acids, enzymes, hormones, antibodies* and *non-protein molecules* such as *nucleic acids*. Unlike carbohydrates and lipids (which can be stored as glycogen and adipose tissue, respectively) there are no storage molecules for amino acids. Some amino acids are metabolised to pyruvate, some to acetyl coenzyme A and others to various intermediates in glucose metabolism. Energy is obtained by their break down into carbon dioxide and water.

17.5. RESPIRATION

Respiration is a process of inhaling of oxygen and exhaling of carbon dioxide by the body. An average adult man inhales about 250 cm^3 of oxygen and exhales about 200 cm^3 of carbon dioxide per minute. The supply of oxygen to tissues and removal of CO_2 are both brought about by blood. It is an energy releasing

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process during which free oxygen combines with glucose and oxidises it to CO_2 and H_2O with the release of energy in the form of ATP.

$$\underset{\text{Glucose}}{C_6H_{12}O_6} + 6O_2 \xrightarrow{\text{Respiration}} 6CO_2 + 6H_2O + \text{Energy (38 ATP)}$$

Carbon dioxide is exhaled out whereas water is retained by the body.

Physiology of respiration. The physiology of respiration can be explained in the following steps :

(*i*) **External respiration.** During this phase, oxygen from the inhaled air diffuses into blood capillaries and CO_2 diffuses out. It occurs in the alveoli of lungs.

(*ii*) **Internal respiration.** During this phase, blood transports oxygen to the cells with the help of oxyhaemoglobin which is formed by the combination of haemoglobin and oxygen in lungs. It occurs in tissues. It also receives CO_2 from the cells through tissue fluid.

(*iii*) **Cell respiration.** In this phase, oxygen is utilised in bringing about oxidation in the cells producing energy, water and CO_2.

Transport of carbon dioxide. The carbon dioxide formed during respiration is transported in three forms :

(*i*) About 80% of CO_2 combines with sodium carbonate of plasma and potassium carbonate of RBC to form corresponding *bicarbonates.*

(*ii*) About 10% of CO_2 dissolves in plasma to form *carbonic acids.*

(*iii*) Rest of CO_2 combines with amino group of haemoglobin to form *carbamino haemoglobin.*

All the above reactions are reversible and therefore, bicarbonates, carbonic acid and carbamino haemoglobin decompose at the respiratory surface to push out CO_2.

17.6. WATER AND BLOOD : THE VITAL FLUIDS

The human body is constituted by many different kind of fluids which have different compositions and are associated with characteristic functions. These particularly concern with the various metabolic activities. Water and blood are two important body fluids and constitute approximately 75% of the total fluids constituting human beings.

WATER

It is the principle fluid of human body. It has distinctive properties like high boiling point (100°C) and dissolves a large variety of both ionic and non-ionic compounds. Almost all body fluids are water solutions.

Water is a medium used for transport of chemicals to and from cells. In each cell, it serves as a medium in which metabolic and biochemical reactions take place. It constitutes approximately 70% of the total body weight. A healthy human adult ingests and excretes about 1.5 to 3.0 litres of water per day. The excretion of water takes place through perspiration, urination, lung exhaltion, etc.

The water balance of a body should be maintained. This is achieved primarily by kidneys which in conjunction with thirst mechanism, control the excretion of water via urination. In diseased state the water balance of the body usually gets upset and this may result either in dehydration (due to frequent excretion) or retention of water (oedema).

BLOOD

It is a bright red (when oxygenated), opaque fluid having a saltish taste and is one of the most important and vital body fluid. This primarily serves as the transporter of oxygen to all body parts and organs through

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the pumping action of heart. An average person has about 6.8 Litres of blood. It forms about 6 – 10% of the body weight.

Composition of Blood. Blood has a complex composition. It consists of a liquid, which contains innumerable *corpuscles* floating in it, called **plasma.**

(*a*) **Plasma.** Plasma forms about 2/3rd or blood. It is a yellowish viscous fluid having following constituents :

(*i*) *Water 90 – 92%*, and

(*ii*) *Plasma proteins.*

The various plasma proteins are *albumin, globulin fibrinogen, prothrombin,* etc.

(*b*) **Corpuscles.** There are three types of corpuscles as described below :

(*i*) *Red blood corpuscles or erythrocytes* (RBC) ;

(*ii*) *White blood corpuscles or leucocytes* (WBC) ; and

(*iii*) *Blood platelets or thrombocytes.*

The main functions of these constituents of blood are listed below in Table 17.1.

Table 17.1

Component	*Function*
1. Plasma solutes	
(*a*) **Electrolytes** (ions) Na^+ and Cl^-	These maintain the osmotic pressure and regulate the fluid balance of body.
HCO_3^-	It helps to regulate the pH of body fluids. It is principal buffer in blood and transports CO_2 from cells to the lungs.
(*b*) **Proteins**	
Albumins	Maintain osmotic pressure of blood plasma and helps in transportation of water insoluble substances (lipids).
Globulins (α, β, γ)	Transport lipids lipoproteins and help in immunology.
Fibrinogen	Blood clotting (protective).
(*c*) **Carbohydrates**	Source of energy which help to maintain body temperature.
2. Blood particles	
(*a*) *Red blood cells (RBC)* Their count in blood is normally between 4.5 – 5.5 million per cubic millimetre of blood. They are red in colour. They contain respiratory pigment haemoglobin.	Transport molecular oxygen from lungs to tissues and CO_2 from tissues to lungs.
(*b*) *White blood cells (WBC)* Their count is about 5000 – 8000 per cubic millimetre.	Defence against infection.
(*c*) *Blood platelets* Their count is approximately 2,50,000 per cubic millimetre.	Blood clotting.

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Haemoglobin (H_b). It is a red pigment and constitutes about 9% of dry mass of blood cells. It is a globular protein. It is made up of four polypeptide chains which are arranged in tetrahedral manner. Each of these chains is associated with non-protein part **haeme** which imparts red colour to the blood.

Function of haemoglobin. In the lungs, there is a high concentration of oxygen. Haemoglobin combines with oxygen to form a bright red compound *oxyhaemoglobin* which is unstable. In fact, oxygen gets attached to iron atom present in haeme. Oxyhaemoglobin is carried by blood stream to various tissues where concentration of oxygen is low. Here, oxyhaemoglobin decomposes to give haemoglobin and oxygen. Oxygen diffuses into cell for carrying out oxidative reactions while haemoglobin returns to the lungs for reuse.

REVIEW QUESTIONS

17.5. Which enzymes start the digestion of food in mouth ?

17.6. Which of the following carbohydrate is not digested by humans ?

(*i*) Starch (*ii*) Cellulose (*iii*) Galactose (*iv*) Glucose

17.7. Which hormone controls the concentration of blood sugar ?

17.8. Which enzymes cause the breakdown of proteins to peptides during digestion ?

17.9. In general, digestion of food is associated with three important phases. What are these ?

17.10. To which disease does excessive retention of water by the body lead to ?

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17.7. IMMUNE SYSTEM

Immunity *is the ability of an organism to resist the development of diseases or effects produced by the entry of some foreign organism or proteins.* ***The defence mechanism of the body to resist infection and poison is called*** **immune system.**

The human immune system is dependent on blood because the lymphocytes present in it produce antibodies or immunoglobulins which fight against the *antigens (harmful germs)*.

Antigens. *These are foreign bodies* (such as bacteria, virus or some protein) *which trigger the production of antibrodies in the body.*

Antibodies. *These are native molecules produced by the body in response to the attack of antigens.* They are ***Y-shaped protein molecules*** having four polypeptides linked together. They are also called **immunoglobulins.**

An the antigen enters the blood, the lymphocytes, a kind of WBC, of blood get attached to these antigens. Each lymphocyte then defends the body by producing protective chemical (antibodies) in responses to the substances released by the antigen in the body. These antibodies further multiply rapidly. Thus, the antibody level in the blood is raised and these make the antigens harmless.

Immunity may be developed in the following ways :

(*i*) **Immunity through disease.** After the first invasion of disease, antibodies (protective cells) are developed in the body. These persist in blood for a long period and prevent the invasion by the same infection again.

(*ii*) **Vaccination.** In this method, weak or dead pathogens or a portion of pathogens (harmful bacteria) are injected into a person who is required to be made immune. These pathogens being weak are unable to cause disease but stimulate the formation of antibolies in the vaccinated person which develops immunity against pathogens.

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Immunity is also achieved by transfer of antibodies from one body to another. For example, nursing mothers transfer antibodies formed in their body to infants through milking the child. Similarly, antibodies for the cure against snake venom (antigen) are obtained from animals like horses and rabbits. The antigen (snake venom) in low dose is injected in horses. The animal then develops antibodies for the antigen. Its blood is then drawn, clotted and the serum left behind contains antibodies. It is then injected for protection against snake bite.

Allergy

Allergy is one of the common problem from which most of the human beings suffer. For instance many persons are sensitive towards medicins like penicillin, sulpha drugs, antibiotics, while others to catfur, dust, pollen grains, particular type of food, or congress grass, etc. **The infavourable reaction of the body to certain substances such as foods, dust, pollens, some drugs, fabric etc.**, is called **allergy.** The substances which cause allergy are called **allergens.** This is due to hypersensitivity of some individuals to allergens which are otherwise harmless. In fact, the body of such hypersensitive persons produce antibodies to these substances. These antibodies then bind the antigens and get attached to the surface of mast cells, a specialised kind of cells. Such a binding then leads these cells to release chemicals such as histamine, seratonin, etc., which induce allergic responses in the body like tissue inflammation, asthma, itching, skin-irritation, etc. Several drugs are available to prevent the production of histamines and combat the allergy effects. These are called **antihistamines.**

17.8. HORMONES

Hormones are **the chemical substances which are produced in the ductless glands in the body.** They are carried to different parts of the body by the blood stream and control various body functions. The ductless glands which produce hormones are called endocrine glands. Some examples of endocrine glands are *the thyroid, the pituitary, the adernals, the pancreas, the testes and the overies.* The endocrine glands secrete these hormones directly into the blood stream through which they reach different parts of the body. In mammals, the secretion of hormones is controlled by the *anterior lobe of the pituitary gland* located at the base of the brain. *The probable function of hormones is to control biological reactions.* However, their exact role is not clearly understood. Hormones are sometimes referred to as **chemical messengers** because of their action to provide among the cells.

Classification of Hormones. On the basis of their chemical constitution, the hormones are divided into three classes :

(*i*) *Steroids* (*ii*) *Proteins or polypeptides* (*iii*) *Amines.*

Steroid Hormones

Steroids are the compounds which are derivatives of four ring system as shown in Fig. 17.2. Sex hormones, bile acids and a number of other biologically active compounds belong to this class.

Steroid alcohols are known as **sterols.** Cholesterol is the most abundant sterol found in animals. It is found in nearly all tissues of the vertebrates and serves as the starting material for synthesizing other steroids. The male sex hormones are secreted by testes and adrenal cortex. *Testosterone* and *androsterone* are examples of male sex hormones. These hormones control the development of reproductive organs and the secondary male characteristics. The female sex hormones *estrone* and *progesterone* are produced by ovaries. These hormones control the menstrual cycle, uterine changes and are involved in the preparation of pregnancy. Some oral contraceptives have been developed that contain synthetic female sex hormones. When these are taken orally, they suppress ovulation.

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The steroids such as cortisone, corticosterone affect metabolism and mineral and water balance. Steroids also occur cardiac-active glycosides in plants as well as in animals. *Digitoxigenin* is a steroid used in the treatment of heart disease. It is extracted from plant digitalis.

Protein or Peptide Hormones

A well known example of this type of hormones is *insulin* which is secreted by pancreas. Its function is to lower the blood sugar level by increasing the rate of conversion of glucose into glycogen. *Oxytocin* and *vasopressin* are the two polypeptide hormones secreted by posterior lobe of the pituitary gland. Oxytocin controls the uterine muscle contraction during child birth. Vasopressin controls the reabsorption of water in kidneys.

Amine Hormones

Thyroxin and *adrenaline (epinephrine)* are the two hormones belonging to this class. Thyroxin is secreted by thyroid and controls the rate of metabolism. Adrenaline is produced by adrenal medula. Its function is reverse of that of insulin. Secretion of adrenaline takes place under the conditions of stress such as fear, anger or some other emergency. It stimulates the glycogenolysis (breakdown of glycogen) in the liver which gives glucose. The glucose thus formed provides the energy necessary to perform physiological work under stress.

Structure of some of the important hormones are given Fig. 17.2.

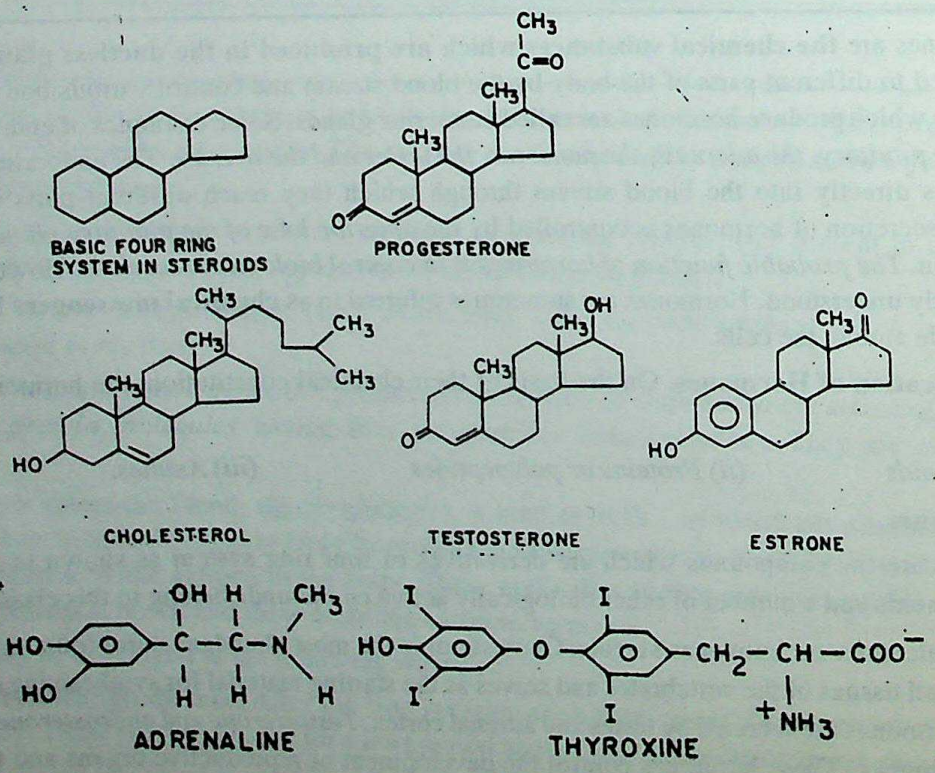

Fig. 17.2. Some Typical Hormones.

The source, chemical nature and function of some hormones are listed in Table 17.2.

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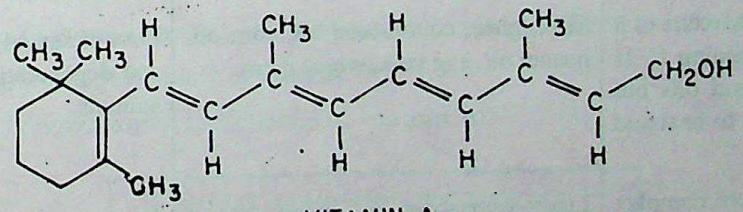
Table 17.2. Some Typical Hormones

Hormone	Source	Chemical Nature	Function
1. Thyroxin	Thyroid	Amino acid	Stimulates metabolism.
2. Adrenaline	Adernal medula	Amine	Increases pulse rate and blood pressure, releases glucose from glycogen and fatty acids from fats.
3. Insulin	Pancreas	Peptide	Decreases blood glucose.
4. Glucogen	Pancreas	Peptide	Increases blood glucose.
5. Testosterone	Testes	Steroid	Controls normal functioning of male sex organs.
6. Estrone and Estradiol	Ovary	Steroid	Controls normal functioning of female sex organs.
7. Progesterone	Ovary	Steroid	Prepares uterus for pregnancy, controls menstrual cycle.
8. Cortisone	Adrenal cortex	Steroid	Metabolism of water, mineral salts, fats, proteins and carbohydrates.

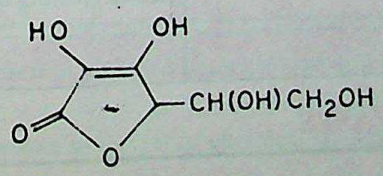
17.9. VITAMINS

The organic compounds other than carbohydrates, proteins and fats that are necessary to maintain normal health, growth and nutrition are called vitamins. It may be noted that vitamins are not used in building cells or as an energy source but they act as catalysis in biological processes, their deficiency causes serious diseases.

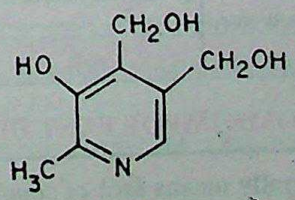
The vitamins are complex organic molecules, however, for the sake of simplicity, they are represented by letters such as A, B, C, D, E, K.



VITAMIN A



VITAMIN C
(ASCORBIC ACID)



VITAMIN B_6
(PYRIDOXINE)

Vitamins are broadly classified into two types, *water soluble vitamins* and *oil soluble vitamins*. Vitamin A, D, E and K are oil soluble whereas vitamins B and C are water soluble. The various vitamins along with their sources and the diseases caused by their deficiencies are listed in Table 17.3.

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Table 17.3. Vitamins and Their Important Sources

Chemical Nature	*Important Sources*	*Deficiency Diseases*
Vitamin A, *Carotenoids.* Soluble in oils and fats, but insoluble in water. It is essential for growth and vision.	Milk, butter, egg yolk, liver, cod liver oil, green and yellow vegetables.	Night blindness, Xerophthalmia (cornea becomes opaque) drying of skin.
Vitamin B_1, *Thiamine.* Soluble in water, destroyed by heat.	Unpolished rice, whole cereals, yeast, egg yolk, liver, milk, green vegetables and fruits.	Beriberi, loss of appetite.
Vitamin B_2, *Riboflavin.* Soluble in water. Stable to heat, destroyed by light.	Egg yolk, liver, milk, green leafy vegetables.	Cracked lips, sore tongue and skin disorders.
Vitamin B_6, *Pyridoxine.*	Cereals, yeast, liver, legumes.	Nervous disturbances and convulsions (*pernious anaemia*).
Vitamin B_{12} or *Cyano Cobalamin.* Soluble in water and contains also cobalt, red crystalline.	Present in all animal tissues. Present in liver, kidney, eggs, beef extract.	A serious type of anaemia.
Vitamin C, *Ascorbic Acid,* $C_6H_8O_6$. Soluble in water, destroyed by cooking and exposure to air. Maintains healthy skin and helps in development of body resistance against diseases.	Oranges, lemons, grapes, tomatoes, cabbage leafy green vegetables, sprouted seeds.	Scurvy, dental caries, pyorrhea, anaemia.
Vitamin D, mixture of 4 complex compounds containing C, H and O. Soluble in fats and oils but insoluble in water. Stable towards heat and oxidation. This vitamin regulates the absorption of calcium and phosphate in intestine.	Cod liver oil, Halibut liver oil and other fish-liver oils. Sun rays catalyse the formation of vitamin D inside the skin, hence called (*sunshine vitamin*).	Infantile rickets; deformation of bones and teeth.
Vitamin E, *Tocopherrol.* Mixture of 3 complex substances containing C, H and O. Soluble in fats and oils but insoluble in water. Stable to heat and oxidation.	Milk, ghee, cotton-seed oil, corn oil, peanut oil, egg yolk, wheat germ.	Loss of sexual power of reproduction and degeneration of muscle fibres in animals.
Vitamin K, mixture of two complex substances containing C, H and O. Soluble in fats but insoluble in water. Stable to heat and oxidation.	Leafy vegetables, fish, meat, oils of grains and cereals.	Tendency to haemorrhage and impaired clotting of blood.

17.10. CHEMISTRY OF SOME IMPORTANT DISEASES

The term *disease* literally means *lack of comfort or uneasiness.* It refers to some kind of disturbance in any organ or malfunction of any part of the body. There are two major types of diseases namely ; *communicable diseases* and *non-communicable diseases* as follows :

Communicable Diseases

These are caused by the entry of disease germs (*pathogens*) into the body and are transmitted from one person to the other by direct or indirect contact. The infection may also spread through water, air, milk, food etc. Depending upon the nature of origin such diseases can be classified as described below :

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1. Viral diseases. These are caused by different viruses. Some examples are : *chicken pox, small pox, measles, poliomyelities, influenza, AIDS, viral hepatitis, rabies and mumps,* etc.

2. Bacterial diseases. These are caused by the infected bacteria present in food and water and also at unhygienical places. The different bacterial diseases are *cholera, typhoid, leprosy, meningitis, tuberculosis,* etc.

3. Venereal diseases. The most common of these are *syphilis* and *gonorrhoea.* These are mostly communicated as a result of sexual intercourse and also with the infected material such as clothes, bedding etc.

4. Protozoal diseases. A few diseases belonging to this category *amoebic dysentery, malaria* etc.

Non-communicable Diseases

The non-communicable diseases, as the name suggests, are not transmitted by contact with a person suffering from a disease or any other agency. They may result from one or more of the following reasons :

(*i*) *the imbalance of essential dietary constitutents* like minerals, salts, vitamins etc.
(*ii*) *general wearing out* or *degeneration of tissues as in old age.*
(*iii*) *uncontrolled growth of tissues in any part of the body.*
(*iv*) *defects in the metabolic reactions.*
(*v*) *injury or damage to any part of the body.*

Some examples of this type of diseases are :

(*i*) *Coronary heart diseases.* These are caused by the insufficient supply of blood to the heat muscles which may result in heart attack.

(*ii*) *Cancer.* It is caused by the uncontrolled growth of cells in any part of the body leading to some sort of tumours.

(*iii*) *Diabetes.* It is caused by the insufficient secretion of the hormone insulin in the pancreas. As a result, the level of sugar in blood increases and it may also pass through urine.

(*iv*) Diseases which are caused by the deficiencies of vitamins are :

Beri-beri (deficiency of vitamin B).

Scurvy, swelling of gums, anaemia etc. (deficiency of vitamin C).

Rickets, osteomalacia (deficiency of vitamin D).

Night blindness, xerphthalmia (deficiency of vitamin A).

SOME IMPORTANT TERMS

- **Anabolism.** It refers to the set of chemical changes which involve the synthesis of macromolecules with in the cell.
- **Catabolism.** It refers to the set of chemical changes which involve the breakdown of macromolecules into smaller ones.
- **Metabolism.** The synthesis and breakdown of macromolecules are collectively called metabolism.
- **ATP** *Adenosinetriphosphate.* It is an energy rich biomolecule which act as centre of all activities of the cell.
- **Photosynthesis.** It is a biochemical process in which carbohydrates are synthesized from carbon dioxide and water in the presence of sun light in plants.
- **Digestion.** It is process of conversion of undiffusable form of food into diffusable or simpler form with the help of enzymes. The digestion mainly occur in mouth, stomach and small intestine.

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- **Respiration.** It is the process of inhaling of oxygen and exhaling of carbon dioxide by the body.
- **Immunity.** It is the ability of the organism to resist the development of diseases or the effects produced by the entry of some foreign organisms.
- **Immune System.** The defence mechanism of the body to resist infection or position.
- **Antigens.** The foreign bodies (such as bacteria, viruses or some proteins) which trigger the production of antibodies in the organism.
- **Antibodies.** The native molecules produced in the body in response to the attack of antigens.
- **Allergy.** The unfavourable reaction of the body in the form of itching, rashes, inflamation, asthma, etc., to certain substances such as food, dust, pollens, some drugs etc.
- **Hormones.** The chemical substances which are produced by the ductless endocrine glands in the body and control various body functions.
- **Vitamins.** The organic compounds other than carbohydrates, proteins and fats which are necessary to maintain normal health, growth and nutrition. They act as catalyst in biological processes.

EXERCISES

VERY SHORT ANSWER QUESTIONS
(1 Mark)

1. Name the enzyme which is present in saliva. What is its important function.
2. What is meant by anabolism ? *(H.P. Board 1994)*
3. What do abbreviations ADP, AMP and ATP represent ?
4. What is the chemical name of vitamin E ?
5. Name the enzymes whose deficiency cause albinism and phenylketone urea. *(CBSE 1990)*
6. Name three enzymes which help in the digestion of food.
7. Name the steroid hormone that regulates the male sex-organs.
8. Which enzyme helps in the digestion of lipids ?
9. What is the function of
   (*i*) Thyroxin (*ii*) Progesterone ?
10. To which category does hormone thiroxin belong ?
11. Name the enzyme which hydrolyse fats into glycerol and fatty acids.
12. What is the cause of goitre ?
13. Which hormones are used by athletes to increase their body weight and strength of muscles ?
14. Name the proteins present in RBC of blood.
15. Which peptide hormone produces milk in mammary glands of women ?
16. Name two chemical substances which produce allergy.
17. Name the two main products of photosynthesis.
18. What is the efficiency of energy conservation in human body ? *(CBSE 1994)*
19. How many molecules of ATP are produced per molecule of glucose in glycolysis. *(CBSE 1994)*
20. What is the role of Vitamin C in our daily life ? *(Pb. Board 1995)*

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DESCRIPTIVE QUESTIONS
(2 Marks)

21. What is meant by the term digestion ? Describe in brief the digestion of proteins and lipids. *[CBSE (3) 1992]*

22. Give structure of adenosine triphosphate indicating clearly the energy rich bonds. Why does its molecule form the source of energy ?

23. In living organism, there are many reactions which have positive value of ΔG, yet they proceed favourably. How do you account for it ?

24. Explain the phenomenon of photosynthesis giving emphasis of light reactions and dark reactions.

25. Describe the digestion of carbohydrates. What is meant by the terms hyperglycemia and hypoglycemia ?

26. What is meant by the terms catabolism, anabolism and metabolism ? Give the brief description of lipid metabolism.

27. Explain the terms :

(*i*) Exergonic reactions (*ii*) Endergonic reactions

(*iii*) Aerobic and anaerobic processes.

28. Give brief description of glucose metabolism.

29. What is water balance of a body and why it should be maintained ?

30. List the important functions of

(*i*) Plasma (*ii*) Blood cells.

31. How is the transport of oxygen maintained in living being ?

32. What is immune system ? How vaccination develops immunity ?

33. Define the terms :

(*i*) Antigens (*ii*) Antibodies.

34. Explain the role played by antibodies to develop immunity ? Discuss it with one example.

35. What is allergy ? What are its causes and how it can be prevented ?

36. Name the vitamin which is essential for proper clotting of blood.

37. What are the body functions with which the following hormones are associated ?

(*i*) Adernaline (*ii*) Insulin (*iii*) Cortisone.

38. Explain light and dark reactions of photosynthesis. *(CBSE 1990)*

39. Explain the term Steroid Hormones and Peptide Hormones. *(CBSE 1990)*

40. What are antibodies ? How do they fight bacteria and virus ? *(CBSE 1992)*

41. Why are vitamin A and vitamin C essential to us ? Give their source. *(CBSE 1992)*

42. Why are vitamins essential to us ? Describe the role of vitamin D in our body. *(CBSE 1992)*

43. What is digestion ? Discuss carbohydrate digestion. *[A.I. CBSE (O) 1992]*

44. Write the principal components of blood along with their main uses. *[Har. (Sc.) 1992]*

45. Describe briefly how glucose works as a source of energy. *(CBSE 1993)*

46. Explain the formation of ATP during photosynthesis. Write reaction step consuming ATP during photosynthesis. *(CBSE 1994)*

47. What is blood ? What is its approx. pH ? Explain the function of haemoglobin. *(Pb. Board 1995)*

48. Explain as to how ATP molecules are regarded as the currency of energy metabolism in cells. *(CBSE 1997)*

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select the correct answer from following questions :

1. ATP represents
   (*a*) abnormal temperature and pressure (*b*) atmospheric temperature
   (*c*) adenosine triphosphate (*d*) none of these.
2. Catabolism refers to
   (*a*) breakdown of complex molecules in living organisms
   (*b*) synthesis of complex molecules
   (*c*) both synthesis as well as breakdown of complex molecules
   (*d*) none of the above.
3. Photosynthesis involves
   (*a*) conversion of chemical energy into radiant energy
   (*b*) conversion chemical energy into mechanical energy
   (*c*) conversion of solar energy into chemical energy
   (*d*) conversion of mechanical energy into chemical energy.
4. Biochemical reactions which require oxygen as called
   (*a*) Metabolic (*b*) Aerobic (*c*) Anaerobic (*d*) No specific name.
5. Hyperglycemia refers to
   (*a*) High blood sugar level (*b*) Low blood sugar level
   (*c*) High conc. of salts in blood (*d*) Low conc. of salts in blood.
6. Which one of following vitamins checks nights blindness ?
   (*a*) A (*b*) B (*c*) C (*d*) D.
7. Which one of the following is synthesized in our body by sun rays ?
   (*a*) Vitamin D (*b*) Vitamin B (*c*) Vitamin K (*d*) Vitamin A.
8. With which of the following disease is vitamin K associated ?
   (*a*) Rickets (*b*) Coagulating property of blood
   (*c*) Scurvy (*d*) Sore throat.
9. The region of plants where photosynthesis occurs is called
   (*a*) Mitochondria (*b*) Chloroplast (*c*) Cytoplasm (*d*) None of the above.
10. In anaerobic respiration, there is a net gain of
    (*a*) 38 ATP (*b*) 50 ATP (*c*) 2 ATP (*d*) 10 ATP.
11. Which name is associated with the chemical substances produced in endocrine ductless glands ?
    (*a*) Vitamins (*b*) Antigens (*c*) Bile acids (*d*) Hormones.
12. During digestion which enzymes convert peptide into amino acids
    (*a*) Peptidase (*b*) Invertase (*c*) Lipase (*d*) Maltase.
13. Which chemical substances act as emulsfiers in lipid metabolism ?
    (*a*) Hydrochloric acid (*b*) Bile acids (*c*) Nucleoside (*d*) Fatty acids.

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14. *Ergoclaciferol* is name of vitamin
(*a*) A (*b*) B (*c*) C (*d*) D.

15. Insulin belong to the category of :
(*a*) Peptide hormones (*b*) Vitamins (*c*) Amine hormone (*d*) Steroid hormone.

FILL IN THE BLANKS

1. Glycolisin of glucose involve breakdown of glucose into .....
2. Vitamin A is mainly found in .....
3. RBC refers to .....
4. Adernaline is secreted by .....
5. The pH of the blood is around .....
6. During photosynthesis of glucose the number of ATP molecules used is .....
7. Silver contains .....
8. The component of blood which functions for blood clotting is .....
9. The unfavourable reaction shown by the body against certain substances is referred to as .....
10. The chemical name of vitamin C is .....

TRUE/FALSE STATEMENTS

Which of the following statements are True or False ?

1. Progestron is a male sex hormon.
2. Adernaline is a steroid hormon.
3. Dark reactions during photosynthesis involve conversion of CO_2 into sugars.
4. The hormone which increase blood glucose level is glucogen.
5. The presence of antigens is the body induces the formation of antibodies.
6. Human gallstones are almost made of calcium carbonate.
7. Cortisone is female sex hormone.
8. Deficiency of vitamin D leads to the disease rickets.
9. Thiamine is a chemical name of vitamin B_{12}.
10. The component of blood which help in immunology and transport lipoproteins is globulins.

MATCHING TYPE QUESTIONS

Match the items of list I, II, and III :

List I	*List II*	*List III*
1. Enzymes	1. Deficiency causes Scurvy	1. Male sex hormone
2. Testosterone	2. Antigen	2. Vitamin C
3. Ascorbic acid	3. Steroid structure	3. Biological catalysts
4. Pepsin	4. Converts proteins to amino acids	4. Defence against infaction
5. Immunoglobulin	5. Globular proteins	5. Digestive enzyme.

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HINTS AND ANSWERS

VERY SHORT ANSWER QUESTIONS

1. Ptyalin ; it hydrolyses starch into maltose.
2. It is a process which involves the synthesis of macromolecules in the cell.
3. Refer to Section 17.1.
4. Toccopherol.
5. Albinism is caused by deficiency of *triosinase*, while phenyl ketone urea is caused by deficiency of *phenylalanine hydroxylase*.
6. *Trypsin, Pepsin, Chymotrypsin.*
7. Testosterone
8. Lipase
10. Amine hormone
11. Lipases
12. Jodine deficiency
13. Anabolic hormones *i.e.*, androgens and estrogens
14. Haemoglobin
15. Oxytocin
16. Histamine and seratonin
17. Carbohydrate and oxygen
18. 38%
19. 36.

MULTIPLE CHOICE QUESTIONS

1. (*c*) 2. (*a*) 3. (*c*) 4. (*b*) 5. (*a*) 6. (*a*)
7. (*a*) 8. (*b*) 9. (*b*) 10. (*c*) 11. (*d*) 12. (*a*)
13. (*b*) 14. (*d*) 15. (*a*)

FILL IN THE BLANKS

1. Pyruvic acid
2. Carrots, cod liver oil
3. RBC
4. Adernal medulla
5. 7.36 to 7.42
6. 18
7. Ptyalin
8. Fibrinogen
9. Allergy
10. ascorbic acid

TRUE/FALSE STATEMENTS

1. False 2. False 3. True 4. True 5. True 6. False
7. False 8. True 9. False 10. True

MATCHING THE COLUMNS

1—5—3, 2—3—1, 3—1—2, 4—4—5, 5—2—4.

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18

Chemistry in Action

LEARNING OBJECTIVES

In this unit, we shall learn about

- *dyes and their applications.*
- *the chemicals in medicine used as antipyretics, analgesics, antiseptics, disinfectants, transquilizers and antibiotics.*
- *the chemicals used as rocket propellants.*

Chemical compounds have been employed for a number of useful purposes in our daily life. For example, sugar is used to sweeten tea, soaps are used for washing and bathing purposes etc. Besides those a number of compounds find application in agriculture, textiles, medicines, photography, etc. The chemicals, thus, play a very important role in our daily life and in a number of biological processes. In this unit, we shall study some important chemical compounds used as dyes, drugs, medicines, rocket propellants, etc.

18.1. DYES

Dyes are the ***chemical substances used to impart colour to fabrics, foods, and other objects for their beautification and distinction.*** They are capable of getting fixed to the fabrics/objects permanently and are resistant to the action of water, soap light, acid, and alkalies.

The colour of dyes is attributed to their ability to absorb some wavelengths of visible region of electromagnetic spectrum (400—750 nm). The part of the light which is reflected back gives the colour of the dye *i.e.*, complementary to the colour absorbed. The colour of visible light absorbed and the complementary colour reflected are listed in Table 18.1.

Table 18.1

Wavelength (nm)	*Colour absorbed*	*Complementary colour*
400—435	Violet	Yellow green
435—480	Blue	Yellow
480—490	Greenish blue	Orange
490—500	Bluish green	Red
500—560	Green	Purple
560—580	Yellowish green	Violet
580—595	Yellow	Blue
595—605	Orange	Greenish blue
605—750	Red	Blue green

In earlier days, as little progress was made in the direction of synthesis of compounds, fabrics were coloured mainly by the dyes obtained from plants. Alizarin (red dye) and indigo (blue dye) are the two common examples of earliest known dyes which were obtained from plants. Now-a-days, many of the natural dyes have been synthesized in the laboratory. The different synthetic routes employed for the preparation of dyes in

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laboratories have helped us to produce dyes of desired shades which otherwise are not available in natural dyes. A wide variety of range of colour and shades are available these days.

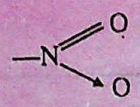
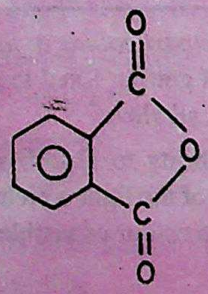
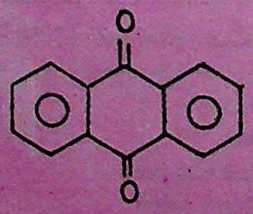
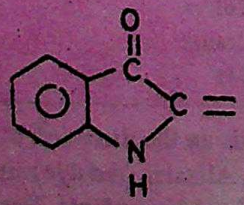
Classification of Dyes

Broadly speaking, the dyes have been classified depending upon :

(*i*) *their chemical constitution,* and (*ii*) *their application to textiles and other purposes.*

(A) Classification Based on Constitution

Depending upon the **characteristic structural units,** constituting the dyes, these are classified as follows :

Type of dye	*Structural unit*	*Examples*
Nitrodyes	 (Nitro group)	Martius yellow, Naphthol yellow.
Azo dyes	—N = N— (azo group)	Orange I, orange II, Congo red.
Triphenyl methane dyes	$(C_6H_5)_3C$— (Triphenyl methane group)	Malachite green, Rosaniline.
Phthaleine dyes	 (Phthalein group)	Phenolphthalein, Mercurochrome.
Anthraquinone dyes	 (Anthraquinone group)	Alizarin
Indigoid dyes	 (Indigoid group)	Indigo, Tyrian purple

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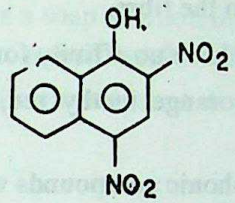
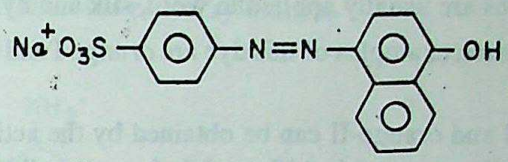
The structures of some common dyes are being given below :

1. Nitro dye



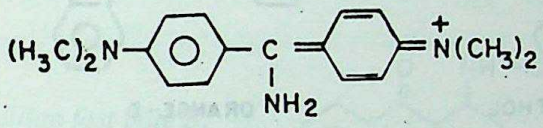
Martius Yellow

2. Azo dye



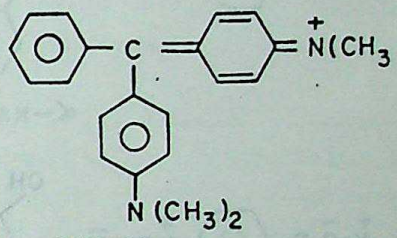
Orange-I

3. Diphenylmethane dye



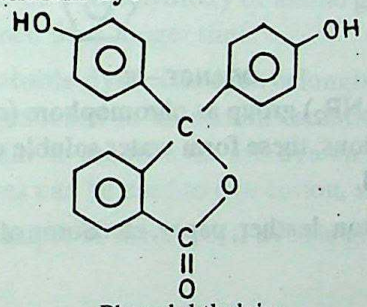
Auromine-O

4. Triphenylmethane dye



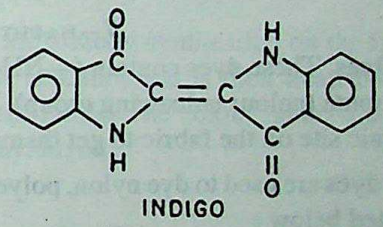
Malachite green

5. Phthalein dye



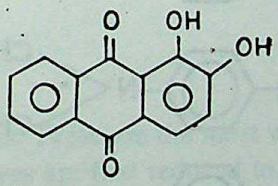
Phenolphthalein

6. Indigoid dye



Indigo

7. Anthraquinone dye



Alizarin

(B) Classification Based on Application

The dyes have also been classified on the basis of their characteristics like fastness of colour, etc., and the kind of fibre these can dye. A particular dye may be suitable for one kind of fibre and may be unsuitable for the other. For example, a dye suitable for wool and silk may not be applied or used for dyeing cotton or rayon. Thus based on the class, shade and other properties like fastness to light, resistance to acids, alkalies, etc., an arbitrary classification of the dyes is done, as given below :

(*a*) *Acid dyes*
(*b*) *Basic dyes*
(*c*) *Direct dyes*
(*d*) *Disperse dyes*
(*e*) *Fibre reactive dyes*
(*f*) *Vat dyes*
(*g*) *Insoluble azo dyes*
(*h*) *Mordant dyes*

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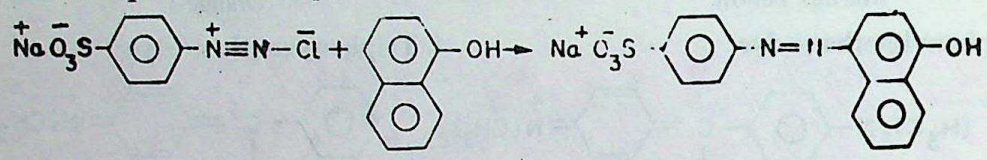
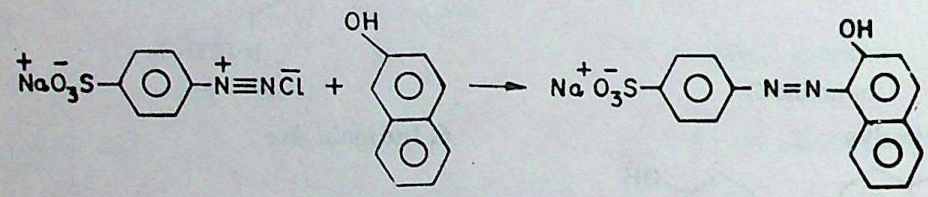
1. Acid dyes. These are azo dyes and are characterized by the presence of acid group like *sulphonic acid (—SO_3H), carboxylic acid (—COOH)* and *phenolic group*. The presence of such groups make the dyes more soluble and also serve as the reactive points for fixing the dye to the fibre.

These dyes are usually applied to wool, silk and nylon. These have no affinity for cotton.

The common examples of this dye are *orange* I and II, methyl orange, methyl red, naphthol blue black 6-B, etc.

Orange-I and orange-II can be obtained by the action of sulphonic compounds with naphthols or by coupling sulphonic compounds with naphthols as described below :

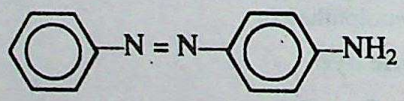




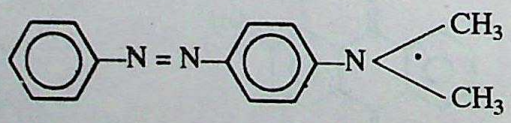
2. Basis Dyes. These dyes contain (—NH_2) group or (—NR_2) group as chromophore (colour bearing group) or auxochrome (colour enhancing group). In acidic solutions, these form water soluble cations. These dyes use the anionic site on the fabric to get themselves attached.

The basic dyes are used to dye nylon, polyester, wool, cotton, leather, paper, etc. Some of the important basic dyes are listed below :

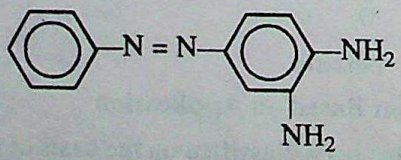
(*i*) *Aniline yellow,*



(*ii*) *Butter yellow,*

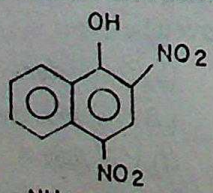


(*iii*) *Crysodine G,*

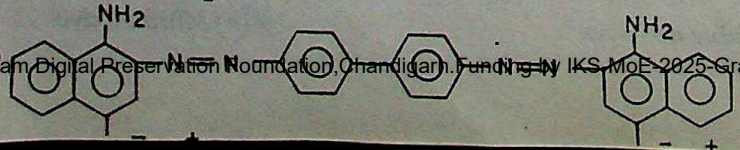


3. Direct dyes. These dyes also belong to the class of azo dyes and are used to dye the fabrics directly by placing it in an aqueous solution of the dye. The direct dyes attack the fibre by means of hydrogen bonding. These are very effective for dying cotton, wool and rayon.

(i) MARTIUS YELLOW,



(ii) CONGO RED,



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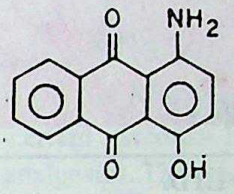
A few examples of the direct dyes are :

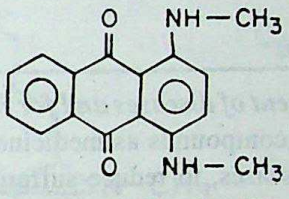
4. Disperse dyes. These dyes, as the name signifies, are usually applied in the form of a dispersion of finely divided dye in a soap solution in the presence of phenol, cresol or benzoic acid. These are mainly used to dye rayon, dacron, nylon, synthetic fibres, polyesters and polyacrylonitrile.

Some common examples of disperse dyes are :

(*i*) *Celliton fast pink B,*



(*ii*) *Celliton fast blue B,*

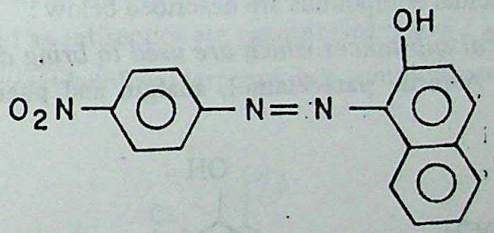


5. Fibre reactive dyes. These dyes are used to dye fibres like cotton, wool or silk. These are linked to the fibre by virtue of the hydroxy or amino group present on the fibre. These dyes induce fast colour on fibres which is retained for a longer time.

6. Insoluble dyes. The dyes belonging to this class are directly synthesised on the fibre. The fabric to be coloured is soaked in an alkaline solution of phenol or naphthol and is then treated with a solution of diazotised amine to produce the azo dye on the surface of the fabric. The colour induced by such dyes is not fast. These dyes can be used to dye cotton, silk, polyester, nylon, etc.

An example of this type of dyes is given below :

Nitroaniline red,



7. Vat dyes. These are the most well-known dyes amongst all others. Before being introduced on to the fabric these dyes are first reduced to colourless leuco compounds in wooden vats by alkaline reducing agent. The fibre is then soaked in the solution of the dye. After the proper absorption of the dye, the fibre is then exposed to air or to an oxidising agent. By doing so the dye gets oxidised to yield insoluble coloured dye on the fabric. *Indigo* is one of the important example of this type of dyes.

8. Mordant dyes. A dye which imparts different colours to the fabric in the presence of different metal ions (called mordants) is referred to as **mordant dye.** This category of dyes have been used from the earlier days. Now-a-days, these dyes are rarely used because superior results can be obtained with other classes of dyes at a low expense and labour.

These dyes are used for dyeing of wool. The method involves the precipitation of certain substances (mordant material) on the fabrics which then combine with the dye to from an insoluble coloured complex called lake. Depending on the kind of mordant used (material designed to bind dye) the dye gives different colours. For example, Alizarin, a mordant dye, gives red colour with aluminium and tin salts, whereas brownish red colour with chromium mordant and black violet with iron mordant.

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REVIEW QUESTIONS

18.1. Does *Auromine O* belong to the category of triphenylmethane dyes ? **Ans.** *No, it is diphenylamine dye.*

18.2. Which is constituting structural unit of orange II ? **Ans.** *—N = N— group.*

18.3. Which is the consituting unit of congo red ? **Ans.** *—N = N— group.*

18.4. Which of the following in a disperse dye ?

(*i*) Celliton fast blue B, (*ii*) Nitroaniline (*iii*) Butter yellow. **Ans.** (*i*)

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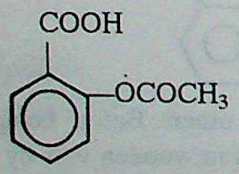
18.2. CHEMICALS IN MEDICINES

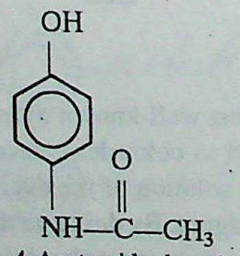
***Chemical substances used for treatment of diseases and for reducing suffering from pain are called* medicines** or **drugs.** Use of some chemical compounds as medicines has helped humanity in a number of ways. Medicines have been used to cure diseases, to reduce suffering from pain and to check population explosion. Medicines have increased the average life span of man and have helped him to lead a comfortable life, free from fear of pain.

The treatment of diseases due to bacterial invasion by chemical compounds which destroy the micro-organism without affecting the tissues of the host is known as **chemotherapy.** The chemicals so used for the cure are called chemotherapeutic agents. Each compound (or chemical) used is specific in its toxicity towards a particular micro-organism. The compounds which exert various physiological effects of therapeutic value are known as drugs. The ideal requirement of the drugs is that on administration (to host) it should be localised at the site where it is required. Medicines are broadly classified according to the purpose for which they are used. Some of the medicinal compounds are described below :

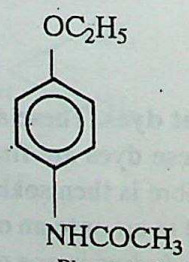
1. Antipyretics. *Chemical substances which are used to bring down the body temperature in high fevers are called antipyretics.* Aspirin, paracetamol, analgin and phenacetin are some of the common antipyretics.



Acetylsalicylic acid
(*Aspirin*)



4-Acetamidophenol
(*para-acetamol*)



Phenacetin

Out of these antipyretics aspirin has been in common use but because on hydrolysis it gives salicylic acid which causes bleeding in stomach, it should not be taken on empty stomach. Calcium and sodium salts of aspirin are more soluble and less harmful.

2. Analgesics. *Chemical substances used for relieving pain are called analgesics.* Aspirin and analgin act both as antipyretics and analgesics.

Novalgin is the most widely used analgesic and has the following structure.

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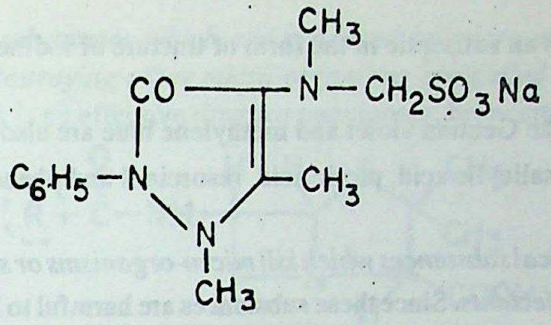
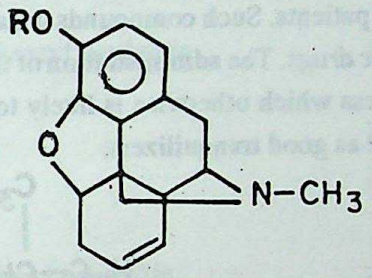
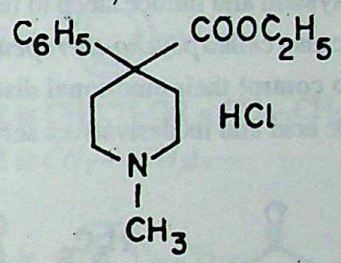


Novalgin

In addition to these analgesics certain narcotics like morphine, codeine, pethidine hydrochloride, methadone, heroin, etc., are also used as analgesics. Though these do relieve the patient of pain but these attack the central nervous system.



R=H, MORPHINE
R=CH3 , CODEINE

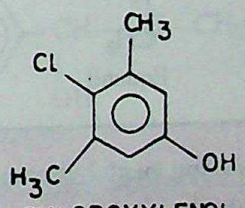


PETHIDINE HYDROCHLORIDE

3. Antiseptics. *Chemical substances which prevent the growth of micro-organisms or kill them but are not harmful to the living human tissues are called antiseptics.* These are applied to wounds, ulcers and diseased skin surfaces. The antiseptics are usually incorporated in face powders, deodorants, breath purifiers, etc., to reduce the odours which may result from the bacterial decomposition on body or in the mouth.

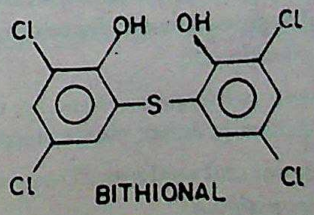
Some of the compounds used as antiseptics are examplified below :

(*i*) *Dettol,* a mixture of chloroxylenol and terpenol, is a commonly used antiseptic for wounds, cuts, diseased skin surfaces, etc.



CHLOROXYLENOL

(*ii*) *Bithional* is added to soaps to impart them antiseptic properties. Such soaps are used to reduce odour due to bacterial action on skin surface.



BITHIONAL

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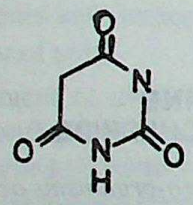
(*iii*) *Iodine* is also used as an antiseptic in the form of tincture of iodine *i.e.* a 2—3% solution of iodine in alcohol-water.

(*iv*) A number of dyes like Gentian violet and methylene blue are also used as antiseptics.

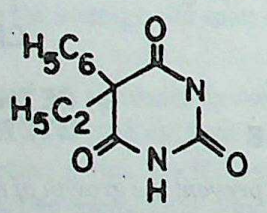
(*v*) In addition to these salicylic acid, picric acid, resorcinol and phenol are also some of the common antiseptics used.

4. Disinfectants. *Chemical substances which kill micro-organisms or stop their growth but are harmful to human tissue are called disinfectants.* Since these substances are harmful to human tissue, hence they cannot be applied directly to wounds. They are used to disinfect floors, toilets, etc. For example, phenol (1%), sulphur dioxide, etc.

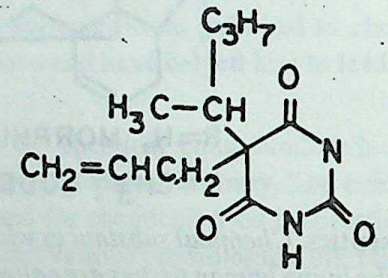
5. Tranquilizers. These are substances which are used for the cure of mental diseases. These effect the central nervous system and induce sleep to the patients. Such compounds usually constitute sleeping pills. The tranquilizers are also called *psycho-therapeutic drugs*. The administration of these drugs makes the patient passive and helps to control their emotional distress which otherwise is likely to interfere with their normal functions. Barbituric acid and its derivatives serve as good tranquilizers.



BARBITURIC ACID

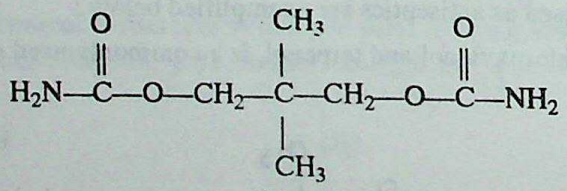


LUMINAL



SECONAL

Equanil is another tranquilizer that is used in depression and hyper tension



Equanil

Different terms associated with drugs for curing mental diseases

Some of the different terms used for the drugs which are used to cure mental diseases are :

1. Sedatives. *These act as depressant and suppress the activities of central nervous system.* They are given to patients who are mentally agitated and violent. Sedatives give a feeling of calmness, relaxation or drowsiness in the body. Their high doses induce sleep. The common sedatives are *valium, barbiturates* (obtained from barbituric acids).

2. Antidepressants. These drugs are given to patients with shattered confidence. These produce a feeling of well being and confidence in the person of depressed mood. Therefore, these are also called mood **booster drugs.** The common examples are *vitalin, cocain, methedrine* etc.

3. Hypnotics. These are also known as *tranquilizers* and are used to reduce mental tension and anxiety. The lower doses of hypnotics or tranquilizers generally do not induce sleep.

4. Narcotics. These act as depressant and analgesic. They reduced tension and anxiety and also reduce pain. The common examples are : *opium, heroin, pethidine.*

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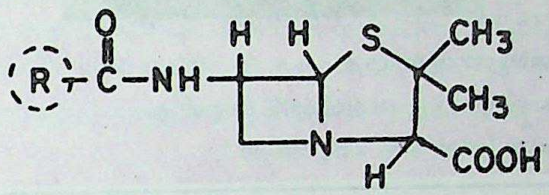
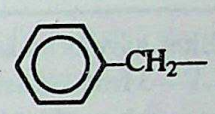
Antibiotics. ***Chemical substances which are produced by micro-organisms (such as moulds and bacteria) and are capable of destroying other micro-organisms are called antibiotics.*** **The first antibiotic discovered was penicillin which is an effective drug for pneumonia, bronchitis, sore throat etc.**



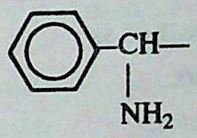
PENICILLIN

With the substitution of different R groups, about six natural penicillins have been isolated so far. There are :

(*i*) ***Penicillin G or Benzyl penicillin*** ; R is 

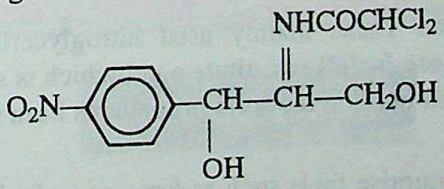
(*ii*) ***Penicillin P*** ; R is $CH_3CH_2CH = CH—CH_2—$

(*iii*) ***Penicillin K*** ; *R is* $CH_2—(CH_2)_6—$

(*iv*) ***Ampicillin or Benzyl penicillin*** ; R is 

Ampicillin **is a modification over penicillin and works against a large number of diseases. However, is several case it induces allergy in the patients. Thus, before it is administered the patients are tested for sensitivity (allergy) to penicillin.**

Choramphenicol **another antibiotic has prolonged action and no sides effects. It is active against diseases caused by spirochetes and viruses as pneumonia. It is also effective in curing relapsing fever, typhoid, dysentry, whooping cough meningitis and certain urinary infections.**



Chloramphenicol

Streptomycin, another antibiotic is used for treatment of tuberculosis. ***Antibiotics which are effective against several different types of harmful micro-organisms*** are called **broad spectrum antibiotics.** Tetracyclins, chloromycetin are examples of such type of antibiotics.

Sulpha drugs also have great antibacterial powers and are used as medicine against various diseases. Their action is also like antibiotics *i.e.* these too protect the body against micro-organisms. When these drugs are administered to patients the bacteria absorb these and cease to grow.

Some important sulpha drugs are :

Sulphadiazine, sulpha thiazole, sulphanilamide, sulpha guanidine, sulpha acetamide, sulpha mezathine, sulpha furazole, sulpha pyridine, etc.

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REVIEW QUESTIONS

18.5. Equanil belongs to which category of drugs ? **Ans.** *Tranquiliser*

18.6. Which is generally added to soap to impart antiseptic properties. **Ans.** *Bithional*

18.7. What type of drugs are used to lower body temperature ? **Ans.** *Antipyretic*

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18.3. CHEMISTRY OF ROCKET PROPELLANTS

A number of satellites have been launched by different countries. India launched its first successful satellite launch vehicle SLV—3 from Sriharikota. In order to push these rocket satellites into the space the lift off of these space vehicles is achieved by having a **propulsion system** in these space vehicles. It comprises rocket engines that are powered with chemicals called **propellants.** The propellant consists of a fuel and an oxidiser. When the propellant is ignited the combustion of fuel occurs with the release of gases which are passed through the nozzle of the rocket motor. This provides the necessary thrust for the rocket uplift.

Propellants are classified as :

(*i*) *solid propellants,* (*ii*) *liquid propellants*, and

(*iii*) *hybrid propellants.*

Solid propellants. They involve the use of **solid fuel** and **solid oxidiser.** They are further divided into two categories.

(*a*) **Composite propellants.** These consist of *polymeric binder,* like polyurethane or polybutadiene, which is used as a *fuel* and ammonium perchlorate which is used as an *oxidiser*. The performance of these propellants can be enhanced by using additives like aluminium or magnesium in the finely divided form with the fuel.

(*b*) **Double base propellants.** These mainly used nitroglycerine and nitro cellulose. In fact, nitroglycerine (liquid) and nitrocellulose (solid) constitute a gel which is semisolid mass, one of the **disadvantage of solid propellants** is that on ignition the solid propellants burn without having a start or stopping capability.

Liquid propellants. These comprise fuels such as *kerosene, alcohol, hydrazine* or *liquid hydrogen* mixed with an oxidiser such as *liquid oxygen, dinitrogen tetraoxide* (N_2O_4) or *nitric acid.* The main **advantage of these propellants** is that (*i*) they give a better thrust than solid propellants. (*ii*) Their thrust can be controlled by regulating the flow of propellants. The *liquid propellant* which consists of two liquids are called **biliquid propellants.** On the other hand, the propellants involving use of single liquid are called **monopropellants.** A number of chemicals like hydrazine, methyl nitrate, nitromethane and hydrogen peroxide are used as **monoproellants.** Among these, except hydrazine (NH_2NH_2) all others serve both as a fuel as well as oxidiser. The other common liquid propellants are unsymmetrical dimethylhdrazine (**UDMH**) and monomethyl hydrazine (**MMH**).

Hybrid rocket propellants. These consist of a solid fuel and a liquid oxidiser. For example, a mixture of a acrylic rubber and liquid dinitrogen tetraoxide.

Propellants used in different space vehicles

(*i*) Saturn booster rocket of American space programme used a combination of liquid oxygen and kerosene as the propellant for initial stage whereas liquid hydrogen and liquid oxygen were used for the upper stage.

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(*ii*) Russian rockets such as Proton used kerosene and liquid oxygen as liquid propellants.

(*iii*) SLV-3 and ASLV, the Indian satellites use composite solid propellants.

(*iv*) For PSL-V rocket yet to be launched, solid propellants are being tried for stage one and third while liquid propellants an N_2O_4 and unsymmetrical dimethyl hydrazine (UDMH) and N_2O_4 and monomethyl hydrazine (MMH) are proposed to be used for the second and fourth stages respectively.

(*v*) For all space shuttles liquid oxygen and liquid hydrogen along with solid boosters are used as propellants.

SOME IMPORTANT TERMS

- **Dyes.** The chemical substances used to imparts colour to wool, silk, food stuff and other objects.
- **Chemotherapy.** It refers to the treatment of diseases by the use of chemicals.
- **Antipyratics.** The substances used to lower body temperature in high fever.
- **Analgesic.** The substances used to relieve pains.
- **Antiseptic's.** The chemical substances which kill or prevent the growth of micro-organisms.
- **Disinfactant.** The chemical substances which are used to kill micro organisms but cannot be applied on living tissues.
- **Antimalarials.** The chemical substances used for treatment of malaria.
- **Tranquilizers.** The chemical substances used to cure mental diseases.
- **Antibiotics.** The chemical substances which are produced by micro-organisms and can inhibit the growth or even destroy other micro organisms.
- **Anaesthetics.** The chemical substances which produce general or local insensibility to pains and other senseations.
- **Propellants.** These are combinations of oxidisers and fuels which on ignition undergo combustion to release large quantities of hot gases, which provide upward thrust to the rocket.

EXERCISES

VERY SHORT-ANSWER TYPE QUESTIONS

1. What do UDMH and MMH stand for ? [*A.I. CBSE (O) Supp. 1990*]
2. Name the chemical responsible for antiseptic properties of dettol. [*A.I. CBSE (O) 1991*]
3. What type of propellant is used in rockets SVL-3 and ASLV ? [*CBSE (3) 1992*]
4. To which category of dyes does alizarin belong ?
5. The dyes which contain (—NO_2) group belong to the cetagory of .....
6. To which type of cloth, the acid dyes are almost ineffective.
7. Name the medicine which can act as analgesic as well as antipyratic. Give its chemical name.
8. Name the chemical substance which can act as antiseptic as well as disinfactant.
9. Give structural formula of aspirin, what is its chemical name ?

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10. Given one example of each of the following :

(*i*) monoliquid propellant (*ii*) azo dye

(*iii*) Antipyretic (*iv*) Acid dye.

11. Give the name of one broad spectrum antibiotic.

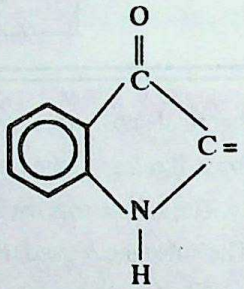
12. How is mordant applied to fabric ? *(CBSE 1994)*

13. Give an example of vat dye. *(CBSE 1994)*

14. Give structure and name of a direct dye. *(Har. Board 1993)*

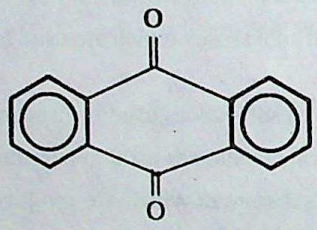
15. Why bithional is added to soap ? *(CBSE 1990)*

16. Write the name and class of dyes having following characteristic unit.



(CBSE 1995)

17. Write the name of dyes having structural unit.



(CBSE 1995)

DESCRIPTIVE QUESTIONS

18. What do you understand by the term dye ? Give name and structure of one dye each belong to

(*i*) vat dyes (*ii*) mordant dyes.

19. Give classification of dyes based on their structural units.

20. Distinguish between acidic and basic dyes.

21. What are Mordant dyes ? How can these be applied to fabrics ? *[CBSE (1) 1992]*

22. Describe an acid dye and an azo dye. *[CBSE (2) 1992]*

23. Explain the following, giving one example each

(*i*) Antipyretics (*ii*) Antiseptics

(*iii*) Broad spectrum antibiotics.

24. Give the structure of the following :

(*a*) Alizarin (*b*) Penicillin

(*c*) Indigo (*d*) Paracetamol.

25. Describe the following with suitable examples.

(*i*) Disinfectant (*ii*) Tranquilizers. *[CBSE (4) 1992]*

26. Why are propellants used in satellites ? Give suitable examples of

(*i*) biliquid propellants (*ii*) hybrid propellants ?

27. What type of propellant is planned to be used in PSLV rocket, yet to be launched ?

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28. Give names of propellants used for

(*i*) Russian satellites (*ii*) American satellites

(*iii*) Indian satellites.

29. What do you understand by the terms

(*i*) Chemotherapy (*ii*) Chemotherapeutic agents.

30. Give classification of dyes based on their applications.

31. Differentiate between direct dyes and disperse dyes.

32. What are (*i*) Solid composite propellants (*ii*) double base propellants ?

33. Explain briefly about the colour of dyes ? What are complementary colours ? Quote two examples.

34. What type of drug is chloramphenicol ? *[A.I. CBSE (O) 1990]*

35. What are basic dyes ? *[A.I. CBSE (O) 1991]*

36. What are biliquid propellants ? What are their advantages over solid propellants ? *(CBSE 1992, 93)*

37. Pick out the odd one from amongst the following compounds on the basis of their medicinal properties mentioning the reason.

Luminal, seconal phenacetin, equanil. *(CBSE 1995)*

38. What is chemotherapy ? Write name of the medicine used for the treatment of the following diseases

(*i*) Tuberculosis (*ii*) Pneumonia (*ii*) High fever. *(Har. Board 1995)*

39. Describe the function of antibiotics and antiseptics. *(Pb. Board 1995)*

40. Pick out the odd one from amongst the following on the basis of their medicinal properties mentioning the reason chloroxylenol Phenol, Chloroamphenicol, Bithional. *(CBSE 1995)*

41. What are the different types of rocked propellants known ? Describe the composition and functioning of one of them. *(CBSE 1997)*

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FOR THE COMPETITIVE EXAMINATIONS

MULTIPLE CHOICE QUESTIONS

Select the correct answer from the questions :

1. Which of the following is an analgesic ?
   (*a*) Chloramphenicol (*b*) Penicillin (*c*) Paracetamol (*d*) Streptomycin.
2. Which of the following is used for the treatment of tuberculosis ?
   (*a*) Penicillin (*b*) Aspirin (*c*) Chloramphenicol (*d*) Streptomycin.
3. Antipyretics are medicinal compounds which
   (*a*) lower body temperature (*b*) relieve pain
   (*c*) control malaria (*d*) can kill other organisms.
4. Asprin is an
   (*a*) analgesic (*b*) antipyretic
   (*c*) antimalarial (*d*) both analgesic and antipyretic.
5. The drug used for treatment of typhoid is
   (*a*) novalgin (*b*) quinine (*c*) chloromycetin (*d*) paracetamol.
6. Chloroquine is a drug which is used to control
   (*a*) pneumonia (*b*) malaria (*c*) pain (*d*) ordinary fever.
7. Streptomycin is specific against
   (*a*) typhoid (*b*) tuberculosis (*c*) malaria (*d*) whooping cough.
8. Which of the following represents a biliquid propellant ?
   (*a*) Nitroglycerine + nitrocellulose (*b*) N_2O_4 + acrylic rubber
   (*c*) N_2O_4 + unsymmetrical dimethylhydrazine (*d*) Polybutadine + ammonium perchlorate.
9. Which of the following is an example of basic dye ?
   (*a*) Alizrin (*b*) Malachite (*c*) Indigo (*d*) Orange-1.
10. SLV-3 rockets use
    (*a*) Solid propellants (*b*) Liquid propellants
    (*c*) Hybrid propellants (*d*) Composite solid propellants.
11. *Veronal*, a barbituric drug is used as
    (*a*) anaesthetic (*b*) sedative (*c*) antiseptic (*d*) none the these.
12. Which of the following is not a chromophore ?
    (*a*) —N = N— (*b*) —NO (*c*) $—NO_2$ (*d*) $—NH_2$.
13. Which of the following is a hypnotic drug ?
    (*a*) Luminal (*b*) Salol (*c*) Catechol (*d*) Phenol.
14. Which of the following is insectiside ?
    (*a*) DDT (*b*) TNT (*c*) TNB (*d*) Aspirin.
15. Which of the following antibiotic contains NO_2 group attached to aromatic nucleus in its structure ?
    (*a*) Penicillin (*b*) Streptomycin (*c*) Chloramphenicol (*d*) All of these.

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FILL IN THE BLANKS

1. Orange-I is an example of ..... dye.
2. UDMH stands for .....
3. In order to give antiseptic properties of soap ..... is added to it.
4. Phenacetin is an ..... drug.
5. Martius yellow belongs to the category of ..... dyes.
6. ..... is mordant dye.
7. The compound used of fix a dye to the fabric is called .....
8. Basic dye contain ..... group.
9. Hydrogen peroxide is ..... propellant.
10. Chemicals used for reducing pain are called .....
11. Synthetic dyes are also called .....
12. Psycotherapeutic drugs are known as .....
13. In composite propellants, the additive used in finely divided .....
14. The mordant generally used for acidic dyes is .....

TRUE/FALSE STATEMENTS

Mark the following statements True or False :

1. Azo dyes are generally produced in *situ*.
2. Penicillin was the first antibiotic discovered.
3. LSD is hallucinogenic drug.
4. Antiseptics are the chemicals used for bringing down the body temperature.
5. Alizrin gives red colour by mordanting it with sulphate of chromium (III) ion.
6. Chemical name of **Aspirin** is 2-Acetoxybenzoic acid.
7. Sulphadiazine is anti-depressant drug.
8. All the Coloured compounds can be used as dyes.
9. Tranquilizers are used for making sleeping pills.
10. The tranquilizer equanil is not a derivative of barbituric acid.
11. Biliquid propellants provide higher thrust than the solid propellants.
12. Chloroquine belongs to the category of antimalarials.
13. The germicide, insecticide *gammaxane* is chemically hexachlorobenzene.
14. Chloroamphenicol is a broad spectrum antibiotic.
15. Indigo belongs to the class of vat dyes.

MATCHING TYPE QUESTIONS

Match the items of Column A and B :

Column A	Column B
1. Chloromycetin	1. Penicillin
2. Alexander flaming	2. $NaO_4(l)$ + Acrylic rubber

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3. Chloroxylenol
4. Hybrid propellant
5. Acetyl salicylic acid
6. Streptomycin
7. Luminal
8. Russiam Rocket (PROTONE)

3. Antibiotic
4. Pain Killer
5. Tranquilizer
6. Typhoid
7. Dettol
8. Kerosene oil + $O_2(l)$

HINTS AND ANSWERS

VERY SHORT ANSWER QUESTIONS

1. UDMH—Unsymmetrical dimethyl hydrazine : MMH—Monomethyl hydrazine
2. Chloroxylenol
3. Solid composite propellant
4. Mordant dyes
5. Nitro dyes
6. cotton cloth
7. Aspirin ; acetylsalicylic acid
8. Phenol
9. $O—(C_6H_4)\begin{cases} OCOCH_3 \\ COOH \end{cases}$
10. Refer text.
11. Streptomycin
12. The fabric to be dyed is soaked in a solution of suitable metal salt (mordant) and subsequently the soaked fabric is dipped in solution of dye. The leads to the formation of coloured complexes on fabric which are known as *lakes*.
13. Indigo
14. Martius yellow
15. To reduce odour produced by bacterial decomposition of organic matter on skin
16. Indigoid dye
17. Anthraquinone dye

MULTIPLE CHOICE QUESTIONS

1. (*c*)	2. (*d*)	3. (*a*)	4. (*d*)	5. (*c*)	6. (*b*)
7. (*b*)	8. (*c*)	9. (*b*)	10. (*d*)	11. (*b*)	12. (*d*)
13. (*a*)	14. (*a*)	15. (*c*)			

FILL IN THE BLANKS

1. azo
2. unsymmetrical dimethyl hydrazine
3. bithional
4. antipyratic
5. nitro
6. alizrine
7. mordant
8. amino
9. monoliquid
10. Analgesics
11. coaltar dyes
12. Tranquilizers
13. Al or Mg
14. Metal ions

TRUE/FALSE STATEMENTS

1. True	2. True	3. True	4. False	5. False	6. True
7. False	8. False	9. True	10. False	11. True	12. False
13. False	14. True	15. True			

MATCHING THE COLUMNS

1—6, 2—1, 3—7, 4—2, 5—4, 6—3., 7—5, 8—8

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APPENDIX I

IMPORTANT TERMS AND COMMON NAMES

A

1. **Adam's** catalyst is Pt/PtO.
2. **Asbestos** is calcium magnesium silicate.
3. **Agate** is silicon dioxide, SiO_2.
4. **Ammonal** is a mixture of ammonium nitrate and Al powder (NH_4NO_3 + Al). It is used as an explosive.
5. **Aqua fortis** is nitric acid, HNO_3.
6. **Antichlor** is sodium thiosulphate. $Na_2S_2O_3.5H_2O$. It is also called **hypo.**
7. **Aqua regia** is a mixture of conc. HNO_3 and conc. HCl in the ratio of 1 : 3. It is also known as **kingly water.**
8. **Alums.** Alums are the substances having general formula $A_2SO_4.B_2(SO_4)_3.24H_2O$ where A is monovalent radical while B is trivalent radical.
9. **Acid salt.** It is a product of partial neutralisation of acid and base in which some of the replaceable H-atoms of the corresponding acids are still present in the salt. For example, $NaHCO_3$, $NaHSO_4$, etc.
10. **Alkali :** A water soluble base is called alkali.
11. **Alloy :** A homogeneous mixture of two or more metals.
12. **Active mass :** It refers to the concentration of the substance in mol L^{-1}.
13. **Amorphous substances.** The substances which donot have orderly arrangement of constituent particles over the long distances.
14. **Aprotic solvent.** Solvents which can neither donate nor accept proton. For example, CCl_4, CS_2. etc.
15. **Artificial rain.** Rain produced by seeding with silver iodide.
16. **Aqua dag :** It is a colloidal solution of graphite in water.

B

17. **Baking soda** is sodium bicarbonate, $NaHCO_3$.
18. **Baryte** is barium sulphate, $BaSO_4$.
19. **Brine** is sodium chloride (NaCl) solution.
20. **Blue vitriol** is copper sulphate, $CuSO_4.5H_2O$.
21. **Bone ash** is mainly calcium phosphate, $Ca_3(PO_4)_2$.
22. **Borax** is sodium tetra borate deca hydrate $Na_2B_4O_7.10H_2O$. Borax ($Na_2B_4O_7$) is also called **tincal.**
23. **Butter of tin** is $SnCl_4.5H_2O$.
24. **B.O.D.** is biological oxygen demand.
25. **Basic salt.** Salt formed by partial neutralisation of a base is called basic salt. *e.g.* Mg(OH)Cl.

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26. **Biodegradable material.** Material which can be broken down or decomposed by bacterial action. *e.g.* Soap is biodegradable but plastics are not.
27. **Bleaching powder** is $CaOCl_2$.
28. **Boron nitride** (BN) is a substance which is as hard as diamond.
29. **Buck minster fullerene.** A recently developed allotrope of carbon with molecular formula C_{60}.
30. **Bigeye Bombs.** The latest chemical weapons fabricated for mass killing.
31. **Bordeaux Mixture.** It is basic copper hydroxide made from $CuSO_4$ and $Ca(OH)_2$ and is important in preventing fungus attack on leaves of potatoes and vines.

C

32. **Caustic soda** is sodium hydroxide NaOH.
33. **Chile salt petre** is sodium nitrate, $NaNO_3$.
34. **Corrosive sublimate** is mercuric chloride, $HgCl_2$.
35. **Chemilumeniscence.** The emission of visible light by means of a chemical reaction.
36. **Carbolic acid** is phenol, C_6H_5OH.
37. **Corundum** is aluminium oxide, Al_2O_3.
38. **Carborundum** is silicon carbide, SiC.
39. **Caro's acid** is peroxymonosulphuric acid, H_2SO_5.
40. **Carbogen** is a mixture of 1% CO_2 and O_2. It is used as antidote for CO poisoning.
41. **Calgon.** It is sodium polymeta phosphate $Na(PO_3)_n$.
42. **Crackling noise.** Certain salts which entrap mother liquor in their crystal structures produce crackling noise when heated in dry conditions. This is due to the escape of mother liquor by dismentling the crystal structure.
43. **Chalcopyrites** is an ore of copper $CuFeS_2$.

D

44. **Dry Ice** is solid carbon dioxide.
45. **Dulong and Petit's rule :** (Atomic mass) × (specific heat) ≈ 6.4.
46. **Deliquescence :** Phenomenon by which certain salts absorb moisture from the air and dissolve in them.
47. **Devarda's alloy** is an alloy of Cu, Al and Zn.
48. **Disproportionation :** Process in which same element increases as well as decreases its oxidation number.

E

49. **Epsom salt** is hepta hydrate magnesium sulphate $MgSO_4.7H_2O$.
50. **Effluorescence :** It is a phenomenon by means of which certain substances give up their water of hydration and disintegrate into dehydrated products.
51. **Euchlorine.** It is a mixture of ClO_2 and Cl_2.

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F

52. **Formalin** is 40% solution of formaldehyde (HCHO).
53. **Fremy's salt** is potassium hydrogen fluoride, KHF_2.
54. **Foul air** is nitrogen, N_2. It is also called **azote.**
55. **Fischer's salt** is potassium cobalt nitrite, $K_3[Co(NO_2)_6]$.
56. **Fowler's solution** is $NaAsO_3$ solution.
57. **Fusion mixture** is a mixture of $Na_2CO_3 + K_2CO_3$.
58. **Fluorine** is called super halogen.
59. **Fluorescence.** It is a process of spontaneous emission of radiations by some substances which are exposed to visible or ultraviolet light.
60. **Fly ash.** A waste product from steel industry. This is added to cement to reduce the cost without affecting the quality.

G

61. **Grain alcohol** is ethyl alochol, C_2H_5OH.
62. **Grape sugar** is Dextrose, $C_6H_{12}O_6$.
63. **Glauber's salt** is sodium sulphate, $Na_2SO_4 . \frac{1}{2}H_2O$.
64. **Gypsum** is calcium sulphate, $CaSO_4.2H_2O$.
65. **Green vitriol** is ferrous sulphate, $FeSO_4.7H_2O$.
66. **Gammexane** is benzene hexachloride (BHC), $C_6H_6Cl_6$.
67. **Gun powder** is a mixture of *sulphur charcoal* and *nitre.*
68. **Graham's salt** is $(NaPO_3)_3$.
69. **Green house gases.** CO_2,CH_4 chlorofluoro carbons etc., cause rise in temperature, *i.e.* globle warming.

H

70. **Heavy hydrogen** is Duterium D_2 or $^2H_2$.
71. **Heavy water** is Duterium oxide, D_2O.
72. **Hard water.** Water which does not produce lather with soap easily.
73. **Hydrolith** is calcium hydride CaH_2.
74. **Halite** is common rock salt (NaCl).

I

75. **Isomorphism** is the phenomenon by virtue of which different compounds possess similar crystalline structures.
76. **Inorganic benzene** is borazole, $B_3N_3H_6$ possessing structure similar to benzene.

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K

77. **King of chemicals** is H_2SO_4.
78. **Kali**-Germans used the word Kali for potash.

L

79. **Lime stone** is calcium carbonate, $CaCO_3$.
80. **Lunar caustic** is silver nitrate, $AgNO_3$.
81. **Laughing gas** is nitrous oxide, N_2O and is also called **laughing grites.**
82. **Lithia water** is aqueous solution of lithium bicarbonate ($LiHCO_3$).
83. **Lapis Lazuli,** is a blue coloured mineral used as semiprecious stone. It is *sodium alumino silicate.*

M

84. **Milk of Magnesia** is magnesium hydroxide, $Mg(OH)_2$.
85. **Muriatic acid** is hydrochloric acid, HCl.
86. **Marshall's acid** is peroxydisulphuric acid, $H_2S_2O_8$.
87. **Magic acid** is $FSO_3H—SbF_5$, one of the strongest acid.
88. **Milk of Lime** is calcium hydroxide, $Ca(OH)_3$. It is also called slaked lime.
89. **Mellitic acid** is $C_6(COOH)_6$.
90. **Microscopic salt** is $Na(NH_4)HPO_4$.
91. **Mica** is $KH_2Al_2(SiO_4)_3$.

N

92. **Nitrolim** is a mixture of CaNCN, (cal. cyanamide) and carbon used as fertilizer.
93. **Norweign salt petre** is basic calcium nitrate, $Ca(NO_3)_2$.
94. **Nessler's reagent** is K_2HgI_4.

O

95. **Oxone** is sodium peroxide, Na_2O_2.
96. **Oil of Vitriol** is sulpuric acid, H_2SO_4.
97. **Oleum** is fuming sulphuric acid, Conc. $H_2SO_4 + SO_3$.

P

98. **Plaster of Pairs** is calcium sulphate hemihydrate, $CaSO_4.1/2H_2O$.
99. **Philosphpher's Wool** is zinc oxide, ZnO.

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100. **Picric acid** is 2, 4, 6-trinitrophenol.
101. **Phosgene** is carbonyl chloride, $COCl_2$.
102. **Paris Green** is double salt of copper acetate and copper arsenate, $Cu(C_2H_8O_2)_2$.
103. **Pearl white** is BiOCl and is used as a pigment.
104. **Prussian blue** is $Fe_4[Fe(CN)_6]_3$.
105. **Prussic acid** is hydrogen cyanide, HCN.
106. **Polymorphism** is existence of given substance in more than one crystalline forms having different physical properties. When elements exhibit polymorphism, it is referred to as **allotropy.**
107. **Protogenic solvents.** The solvents which have tendency to give up protons.
108. **Phosphorescence.** The phenomenon by virtue of which certain substances called **phosphores** continue emitting visible radiation even after the source of radiation to which they have been exposed is removed.
109. **Pearl Ash** is potash used as fertilizer.
110. **Purple of Cassius** is colloidal solution of gold.
111. **Pseudohalide ions** are CN^-, CNO^-, N_2^- etc.

Q

112. **Quartz** is silicon dioxide, $SiCO_2$.
113. **Quick silver** is mercury, Hg.
114. **Quick lime** is calcium oxide, CaO.

R

115. **R.D.X.** It is an explosive called cyclonite.
116. **Rectified spirit** is 95% ethyl alochol, C_2H_5OH.
117. **Rochlle salts** is sodium potassium tartrate, $NaKC_4H_2O_6$.
118. **Red lead** is lead tetroxide, Pb_3P_4.
119. **Red liquor** is aluminium acetate, $(CH_3COO)_3Al$.
120. **Reagar** is As_4S_4.
121. **Rubies and sapphiers** are chemically Al_2O_3.

S

122. **Stranger gas** is xenon (Xe).
123. **Soda lime** is a mixture of NaOH and CaO.
124. **Seildlitz powder** is $NaHCO_3$.
125. **Sterling silver** is a solution of Cu in Ag.
126. **Spirit of salt** is HCl.
127. **Super phosphate of lime** contains $Ca(H_2PO_4)_2H_2O$ and $2CaSO_4.2H_2O$.
128. **Soda ash** is sodium carbonate, Na_2CO_3.

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129. **Smelling salt** is $(NH_4)_2CO_3$.
130. **Scheeb's green** is $CuHAsO_3$.
131. **Sugar of lead** is lead acetate, $(CH_3COO)_2$ Pb.
132. **Sand** is silicon dioxide, SiO_2.
133. **Salt cake** is sodium sulphate, Na_2SO_4.

T

134. **T.N.T.** is trinitrotoluene, an explosive.
135. **Tear gas is chloropicrin,** $CCl_3.NO_2$.
136. **TEL** is tetra ethyl lead, $Pb(C_2H_5)_4$.
137. **Talc** is Magnesium silicate $3MgO.4\ SiO_2H_2O$.
138. **Thomas slag** is calcium phosphate, $Ca_3(PO_4)_2$.
139. **Tincture of Iodine** is I_2 + KI solution in alcohol.
140. **Thermite** is a mixture of iron oxide (Fe_3O_4) and Al powder.
141. **Therapeutic Index.** It is a ratio of the amount of drug necessary to kill the patient, *i.e.* maximum tolerated dose MTD to the minimum curative dose MCO.
142. **Tincry.** The sound produces while bending the tin rod.

V

143. **Vinegar** is dilute acetic acid, CH_3COOH.
144. **Verdigris** is basic copper acetate.

W

145. **Washing soda** is Na_2CO_3.
146. **Water glass** is sodium silicate, Na_2SiO_3.
147. **White lead** is $Pb(OH)_2.2PbCO_3$.
148. **Wackenroder's liquid** is $H_2SO_4 + H_2S$.
149. **White Vitriol** is zinc sulphate, $ZnSO_4.7H_2O$.

Z

150. **Zieggler's Natta Catalyst** $TiCl_4/Al(C_2H_5)_3$.
151. **Ziez's Salt** $K[PtCl_3^{-n2} - (C_2H_4)]$.

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APPENDIX II

SAMPLE PAPER NO. 1

Time : 3 hrs. *M.M. 70*

General Instructions :

1. *All questions are compulsory.*
2. *Question numbers 1 to 10 are very short answer questions. Answer them in about one sentence each.*
3. *Question numbers 11 to 26 are short-answer questions. Answer them in not more than 30 words each.*
4. *Question numbers 27 to 32 are also short-answer questions. Answer them in not more than 140 words each.*
5. *Question numbers 33 and 34 are long answer questions. Answer them in not more than 70 words.*

1. Why there are no *f*-orbitals in first energy level ? 1

2. Give one example of ferrimagnetic substances. 1

3. What do you understand by 'kinetically stable reactants' ? 1

4. Give structural formula of phosphorus acid. 1

5. Which of Zn^{2+} and Cu^{2+} has higher magnetic moment and why ?
(At No. of Zn = 30 and Cu = 29) 1

6. Give IUPAC name of the compound : $Fe_4[Fe(CN)_6]_3$. 1

7. Give equation for the first artificial transmutation carried out in laboratory. 1

8. Explain why extent of adsorption of a gas on a solid surface increases with increase in specific area of the solid. 1

9. Name the bases present in RNA. 1

10. What is gold number ? 1

11. Assuming that a 100 watt bulb emits monochromatic light of wavelength 6000 A. Calculate the rate of emission of quanta per second. 2

12. KF has rock-salt structure. Calculate its density from the information give below :
Distance between K^+ and F^- ions in KF = 268 pm
Avogadro's number = 6.02×10^{23}. 2

13. Entropy of vaporisation of acetone is 93.00 JK^{-1} mol^{-1}. Calculate the heat required for vaporisation of 1 g of acetone. Given that
Boiling point of acetone = 56°C
Molar mass of acetone = 46 g. 2

14. State the following : 2
1. Molar conductance 2. Kohlrausch law

15. Calculate the EMF of the cell in which the cell reaction is

$$Mg + 2Ag^+(aq) \longrightarrow Mg^{2+}(aq) + 2Ag$$

which $|Mg^{2+}| = 0.130$ M and $|Ag^+| = 1.00 \times 10^{-4}$ M

$E^\circ_{Mg^{2+}/Mg} = -2.37$ V, $E^\circ_{Ag^+/Ag} = 0.7994$ V 2

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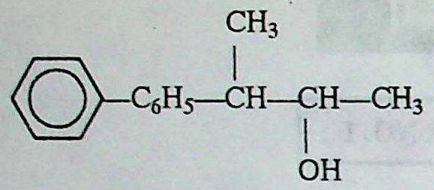
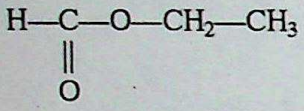
16. Give IUPAC names of the following compounds

1. 

2. 

2

17. Explain the following reactions :

1. Diazotisation
2. Hoffmann bromide reaction. 2

18. How would you convert benzene into 1-bromo 3-chloro benzene ? 2

19. Explain why elements of 5-*d* transition series have higher ionisation energies than the corresponding elements of 3-*d* and 4-*d* transition series. 2

20. What is inert pair effect ? Explain with the help of some examples. 2

21. The Rb-87 to Sr-87 method of dating rocks was used to analyse lunar rocks. Estimate the age of the rock in which the mole ratio of Rb-87 to Sr-87 is 25.0.

$$t_{1/2} = 5.7 \times 10^{10} \text{ years.}$$ 2

22. Write short note on Hardy-Schulze rule. 2

23. Describe the formation of Nylon-6 starting from cyclohexane. 2

24. Name the diseases caused by deficiency of enzymes phenylalanine hydroxylase and triosinase. 2

25. Describe the process of photo synthesis, clearly indicating the light reactions and dark reactions. 2

26. Write short note on vat dyes. 2

27. State second law of thermodynamics. How is spontaneity of process predicted with the help a thermodynamic function of the system ? 3

28. For a first order reaction, the factor A in the Arrhenius equation has a value of $1.0 \times 10^{14} s^{-1}$ and E_{act} is 80 kJ/mole. Calculate how many times the rate of this reaction increases when temperature is raised from 300 K to 310 K.

29. How will you carry out the following conversions ?

1. Acetone into acetic acid 2. 2-Propanol into *n*-hexane. 3

30. Account for the following :

1. Aldehydes are more easily oxidised then ketones 3
2. Ethyl amine is more basic than aniline. 3

31. Describe the following :

1. A test to distinguish between primary, secondary and tertiary amines.
2. Amphoteric character of amides. 3

32. (*a*) Write short note on lanthanide contraction.

(*b*) Explain the bonding in tetracyano nicklate (II) ion on the basis of Valance Bond Theory. Predict the shape and magnetic behaviour of this complex ion. 1 + 2 = 3

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33. Discuss general characteristics of group-14 elements. What are silicones ? Give their uses. 5

34. (*a*) State Raoult's law. Draw vapour pressure graphs for a solution containing two miscible, volatile liquids, assuming that the solution obeys.Raoult's law.

(*b*) Solution of two volatile liquids A and B obeys Raoult's law. At a certain temperature it is found that when the total pressure above the given solution is 400 mm, the mole fraction of A in the vapours is 0.45 and in the liquid is 0.65. What are the vapour pressure of the two pure liquids.

2 + 3 = 5

SAMPLE PAPER NO. 2

Time Allowed : 3 hrs. *Maximum Marks : 70*

General Instructions :

(*i*) *All questions are compulsory.*

(*ii*) *Marks for each question are indicated against it.*

(*iii*) *Question numbers 1 to 10 are very short-answer questions each of 1 mark. Answer them in about one sentence each.*

(*iv*) *Question number 11 to 26 are short-answer questions of 2 marks each. Answer them in not more than 30 words each.*

(*v*) *Question numbers 27 to 32 are short-answer questions of 3 marks each. Answer them in not more than 40 words each.*

(*vi*) *Question numbers 33 and 34 are long-answer questions of 5 marks each. Answer them in not more than 70 words each.*

(*vii*) *Use Log Tables, if necessary.*

1. Why do transition elements shown variable oxidation states ? 1
2. State Pauli's exclusion principle. 1
3. Which quantum number specifies the shape of an orbital ? 1
4. What is the effect of decreasing concentration on the molar conductivity of a weak electrolyte ? 1
5. How is ferromagnetism different from paramagnetism ? 1
6. Why is the osmotic pressure considered to be a colligative property ? 1
7. Mention two uses of glycerol. 1
8. Mention the chief use of quaternary ammonium salts derived from long chain tertiary amines. 1
9. What is the efficiency of energy conversion in human body ? 1
10. Give an example of vat dye. 1
11. The form of the rate law for a reaction is expressed as

$$\text{rate} = k\,[Cl_2][NO]^2$$

Find out the orders of reaction with respect to Cl_2 and with respect to NO and also the overall order of the reaction. 2

12. With the help of molecular orbital approach show that Ne_2 cannot exist as a stable species. 2

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13. An element (atomic mass = 60) having face-centred cubic structure has a density of 6.23 g cm^{-3}. What is the edge length of the unit cell ?

(Avogadro constant, $N = 6.02 \times 10^{23}$ mol^{-1}) 2

14. A reaction that is first order with respect to reactant A has a rate constant of 6 min^{-1}. If we start with [A] = 5.0 mol L^{-1}, when would [A] reach the value of 0.05 mol L^{-1} ? 2

15. At 298 K, 100 cm^3 of a solution containing 3.02 g of an unidentified solute exhibits an osmotic pressure of 2.55 atmospheres. What is the molecular mass of solute ?

($R = 0.0821$ L atm mol^{-1} K^{-1}) 2

16. Calculate the number of coulombs required to deposit 6.75 g of Al when electrode reaction is

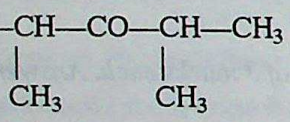
$$Al^3 + 3e^- \longrightarrow Al.$$

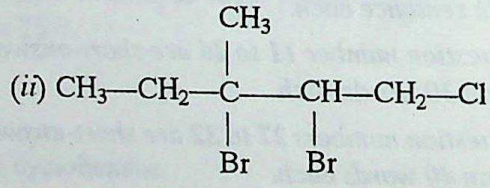
(Given : Atomic mass Al = 27 g mol^{-1}, F = 96,500 C mol^{-1}) 2

17. Define vapour pressure of a liquid. What happens to the vapour pressure when (*a*) a volatile solute dissolves in the liquid and (*b*) the dissolved solute is non-volatile ? 2

18. The enthalpy change for the transition of liquid water to steam (ΔH_{vap}) is 40.8 kJ mol^{-1} at 373 K. Calculate the entropy change (ΔS_{vap}) of the process. 2

19. Give the IUPAC names for the following compounds :

(*i*) 

(*ii*)  2

20. What happens when

(*i*) methylamine is heated with chloroform in the presence of an alkali.

(*ii*) a mixture of alcohol and ammonia in vapour state is passed over heated aluminium oxide as catalyst ? 2

21. Giving an appropriate examples to explain how the presence of a substituent on aliphatic chain of a carboxylic acid affects its acidic strength. 2

22. How can you obtain :

(*i*) Iodoform from propanone

(*ii*) 2-propanol from ethanol 2

23. Explain the mechanism of the following reaction

$$2C_2H_5OH \xrightarrow[413\ K]{conc.\ H_2SO_4} C_2H_5OC_2H_5 + H_2O.$$ 2

24. Of benzene and phenol, which is more easily nitrated and why ? 2

25. How will you account for the following :

(*i*) It is difficult to prepare pure amines by ammonolysis of alkyl halides

(*ii*) Chloroacetic acid is a stronger acid then acetic acid. 2

26. What are fuel cells ? Write the reaction of a oxygen-hydrogen fuel cell. 2

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27. Complete the following nuclear reactions :

(*i*) ..... $(\alpha, 2n)\ ^{211}_{85}At$ (*ii*) $^{96}_{42}Mo$ (....., n) $^{97}_{83}Tc$

(*iii*) $^{55}_{25}Mn$ (n, γ). 3

28. List three functions of nucleotides in a cell. 3

29. Answer the following :

(*i*) How is mordant dye applied to fabrics ?

(*ii*) What is achieved energetically by coupling of reactions ?

(*ii*) What is the principle of dialysis ? 3

30. Briefly describe the following terms giving one example of each :

(*i*) Polyolefins (*ii*) Polyamides

(*iii*) Polyesters. 3

31. Describe the following terms while stating the properties of colloids :

(*i*) Electrophoresis (*ii*) Brownian movement

(*iii*) Tyndall effect. 3

32. Discuss the structure of each of the following :

(*i*) Cis—$[Pt(NH_3)_2Cl_2]$ (*ii*) $[Co(NH_3)_6]^{3+}$

(*iii*) Ferrocene. 3

33. (*a*) Write the balanced equation for the following reactions :

(*i*) $SbCl_3 + H_2O \longrightarrow$ (*ii*) $IO_3^- + I^- + H^- \longrightarrow$

(*iii*) $XeF_4 + SbF_5 \longrightarrow$

(*b*) Arrange the following in the increasing order of the property indicated :

(*i*) KCl, $MgCl_2$, $CaCl_2$, $BeCl_2$—ionic character

(*ii*) PH_3, NH_3, SbH_3, AsH_3—base strength. 5

34. Describe the general characteristics or transition elements with special reference to the following :

(*i*) Complex formation (*ii*) Enthalpies of atomisation

(*iii*) Variable oxidation states (*iv*) Formation of coloured ions

(*v*) Interstitial compounds. 5

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						2672	2695	2718	2742	2765	2	4	7	9	11	14	16	18	21
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31	4914	4928	4942	4955	4969	4983	4997	5011	5024	5038	1	3	4	6	7	8	10	11	12
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.18	1514	1517	1521	1524	1528	1531	1535	1538	1542	1545	0	1	1	1	2	2	2	3	3
.19	1549	1552	1556	1560	1563	1567	1570	1574	1578	1581	0	1	1	1	2	2	3	3	3
.20	1585	1589	1592	1596	1600	1603	1607	1611	1614	1618	0	1	1	1	2	2	3	3	3
.21	1622	1626	1629	1633	1637	1641	1644	1648	1652	1656	0	1	1	2	2	2	3	3	3
.22	1660	1663	1667	1671	1675	1679	1683	1687	1690	1694	0	1	1	2	2	2	3	3	3
.23	1698	1702	1706	1710	1714	1718	1722	1726	1730	1734	0	1	1	2	2	2	3	3	4
.24	1738	1742	1746	1750	1754	1758	1762	1766	1770	1774	0	1	1	2	2	2	3	3	4
.25	1778	1782	1786	1791	1795	1799	1803	1807	1811	1816	0	1	1	2	2	2	3	3	4
.26	1820	1824	1828	1832	1837	1841	1845	1849	1854	1858	0	1	1	2	2	3	3	3	4
.27	1862	1866	1871	1875	1879	1884	1888	1892	1897	1901	0	1	1	2	2	3	3	3	4
.28	1905	1910	1914	1919	1923	1928	1932	1936	1941	1945	0	1	1	2	2	3	3	4	4
.29	1950	1954	1959	1963	1968	1972	1977	1982	1986	1991	0	1	1	2	2	3	3	4	4
.30	1995	2000	2004	2009	2014	2018	2023	2028	2032	2037	0	1	1	2	2	3	3	4	4
.31	2042	2046	2051	2056	2061	2065	2070	2075	2080	2084	0	1	1	2	2	3	3	4	4
.32	2089	2094	2099	2104	2109	2113	2118	2123	2128	2133	0	1	1	2	2	3	3	4	4
.33	2138	2143	2148	2153	2158	2163	2168	2173	2178	2183	0	1	1	2	2	3	3	4	4
.34	2188	2193	2198	2203	2208	2213	2218	2223	2228	2234	1	1	2	2	3	3	4	4	5
.35	2239	2244	2249	2254	2259	2265	2270	2275	2280	2286	1	1	2	2	3	3	4	4	5
.36	2291	2296	2301	2307	2312	2317	2323	2328	2333	2339	1	1	2	2	3	3	4	4	5
.37	2344	2350	2355	2360	2366	2371	2377	2382	2388	2393	1	1	2	2	3	3	4	4	5
.38	2399	2404	2410	2415	2421	2427	2432	2438	2443	2449	1	1	2	2	3	3	4	4	5
.39	2455	2460	2466	2472	2477	2483	2489	2495	2500	2506	1	1	2	2	3	3	4	5	5
.40	2512	2518	2523	2529	2535	2541	2547	2553	2559	2564	1	1	2	2	3	4	4	5	5
.41	2570	2576	2582	2588	2594	2600	2606	2612	2618	2624	1	1	2	2	3	4	4	5	5
.42	2630	2636	2642	2649	2655	2661	2667	2673	2679	2685	1	1	2	2	3	4	4	5	6
.43	2692	2698	2704	2710	2716	2723	2729	2735	2742	2748	1	1	2	3	3	4	4	5	6
.44	2754	2761	2767	2773	2780	2786	2793	2799	2805	2812	1	1	2	3	3	4	4	5	6
.45	2818	2825	2831	2838	2844	2851	2858	2864	2871	2877	1	1	2	3	3	4	5	5	6
.46	2884	2891	2897	2904	2911	2917	2924	2931	2938	2944	1	1	2	3	3	4	5	5	6
.47	2951	2958	2965	2972	2979	2985	2992	2999	3006	3013	1	1	2	3	3	4	5	5	6
.48	3020	3027	3034	3041	3048	3055	3062	3069	3076	3083	1	1	2	3	4	4	5	6	6
.49	3090	3097	3105	3112	3119	3126	3133	3141	3148	3155	1	1	2	3	4	4	5	6	6

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ANTILOGARITHMS

	0	1	2	3	4	5	6	7	8	9	1	2	3	4	5	6	7	8	9
.50	3162	3170	3177	3184	3192	3199	3206	3214	3221	3228	1	1	2	3	4	4	5	6	7
.51	3236	3243	3251	3258	3266	3273	3281	3289	3296	3304	1	2	2	3	4	5	5	6	7
.52	3311	3319	3327	3334	3342	3350	3357	3365	3373	3381	1	2	2	3	4	5	5	6	7
.53	3388	3396	3404	3412	3420	3428	3436	3443	3451	3459	1	2	2	3	4	5	6	6	7
.54	3467	3475	3483	3491	3499	3508	3516	3524	3532	3540	1	2	2	3	4	5	6	6	7
.55	3548	3556	3565	3573	3581	3589	3597	3606	3614	3622	1	2	2	3	4	5	6	7	7
.56	3631	3639	3648	3656	3664	3673	3681	3690	3698	3707	1	2	3	3	4	5	6	7	8
.57	3715	3724	3733	3741	3750	3758	3767	3776	3784	3793	1	2	3	3	4	5	6	7	8
.58	3802	3811	3819	3828	3837	3846	3855	3864	3873	3882	1	2	3	4	4	5	6	7	8
.59	3890	3899	3908	3917	3926	3936	3945	3954	3963	3972	1	2	3	4	5	5	6	7	8
.60	3981	3990	3999	4009	4018	4027	4036	4046	4055	4064	1	2	3	4	5	6	6	7	8
.61	4074	4083	4093	4102	4111	4121	4130	4140	4150	4159	1	2	3	4	5	6	7	8	9
.62	4169	4178	4188	4198	4207	4217	4227	4236	4246	4256	1	2	3	4	5	6	7	8	9
.63	4266	4276	4285	4295	4305	4315	4325	4335	4345	4355	1	2	3	4	5	6	7	8	9
.64	4365	4375	4385	4395	4406	4416	4426	4436	4446	4457	1	2	3	4	5	6	7	8	9
.65	4467	4477	4487	4498	4508	4519	4529	4539	4550	4560	1	2	3	4	5	6	7	8	9
.66	4571	4581	4592	4603	4613	4624	4634	4645	4656	4667	1	2	3	4	5	6	7	9	10
.67	4677	4688	4699	4710	4721	4732	4742	4753	4764	4775	1	2	3	4	5	7	8	9	10
.68	4786	4797	4808	4819	4831	4842	4853	4864	4875	4887	1	2	3	4	6	7	8	9	10
.69	4898	4909	4920	4932	4943	4955	4966	4977	4989	5000	1	2	3	5	6	7	8	9	10
.70	5012	5023	5035	5047	5058	5070	5082	5093	5105	5117	1	2	4	5	6	7	8	9	11
.71	5129	5140	5152	5164	5176	5188	5200	5212	5224	5236	1	2	4	5	6	7	8	10	11
.72	5248	5260	5272	5284	5297	5309	5321	5333	5346	5358	1	2	4	5	6	7	9	10	11
.73	5370	5383	5395	5408	5420	5433	5445	5458	5470	5483	1	3	4	5	6	8	9	10	11
.74	5495	5508	5521	5534	5546	5559	5572	5585	5598	5610	1	3	4	5	6	8	9	10	12
.75	5623	5636	5649	5662	5675	5689	5702	5715	5728	5741	1	3	4	5	7	8	9	10	12
.76	5754	5768	5781	5794	5808	5821	5834	5848	5861	5875	1	3	4	5	7	8	9	11	12
.77	5888	5902	5916	5929	5943	5957	5970	5984	5998	6012	1	3	4	5	7	8	10	11	12
.78	6026	6039	6053	6067	6081	6095	6109	6124	6138	6152	1	3	4	6	7	8	10	11	13
.79	6166	6180	6194	6209	6223	6237	6252	6266	6281	6295	1	3	4	6	7	9	10	11	13
.80	6310	6324	6339	6353	6368	6383	6397	6412	6427	6442	1	3	4	6	7	9	10	12	13
.81	6457	6471	6486	6501	6516	6531	6546	6561	6577	6592	2	3	5	6	8	9	11	12	14
.82	6607	6622	6637	6653	6668	6683	6699	6714	6730	6745	2	3	5	6	8	9	11	12	14
.83	6761	6776	6792	6808	6823	6839	6855	6871	6887	6902	2	3	5	6	8	9	11	13	14
.84	6918	6934	6950	6966	6982	6998	7015	7031	7047	7063	2	3	5	6	8	10	11	13	15
.85	7079	7096	7112	7129	7145	7161	7178	7194	7211	7228	2	3	5	7	8	10	12	13	15
.86	7244	7261	7278	7295	7311	7328	7345	7362	7379	7396	2	3	5	7	8	10	12	13	15
.87	7413	7430	7447	7464	7482	7499	7516	7534	7551	7568	2	3	5	7	9	10	12	14	16
.88	7586	7603	7621	7638	7656	7674	7691	7709	7727	7745	2	4	5	7	9	11	12	14	16
.89	7762	7780	7798	7816	7834	7852	7870	7889	7907	7925	2	4	5	7	9	11	13	14	16
.90	7943	7962	7980	7998	8017	8035	8054	8072	8091	8110	2	4	6	7	9	11	13	15	17
.91	8128	8147	8166	8185	8204	8222	8241	8260	8279	8299	2	4	6	8	9	11	13	15	17
.92	8318	8337	8356	8375	8395	8414	8433	8453	8472	8492	2	4	6	8	10	12	14	15	17
.93	8511	8531	8551	8570	8590	8610	8630	8650	8670	8690	2	4	6	8	10	12	14	16	18
.94	8710	8730	8750	8770	8790	8810	8831	8851	8872	8892	2	4	6	8	10	12	14	16	18
.95	8913	8933	8954	8974	8995	9016	9036	9057	9078	9099	2	4	6	8	10	12	15	17	19
.96	9120	9141	9162	9183	9204	9226	9247	9268	9290	9311	2	4	6	8	11	13	15	17	19
.97	9333	9354	9376	9397	9419	9441	9462	9484	9506	9528	2	4	7	9	11	13	15	17	20
.98	9550	9572	9594	9616	9638	9661	9683	9705	9727	9750	2	4	7	9	11	13	16	18	20
.99	9772	9795	9817	9840	9863	9886	9908	9931	9954	9977	2	5	7	9	11	14	16	18	20

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ATOMIC MASSES OF ELEMENTS REFERRED TO $^{12}C = 12.0000$ amu

Element	*Symbol*	*Atomic Number*	*Atomic mass*
ACTINIUM	Ac	89	(227)
ALUMINIUM	Al	13	27.0
AMERICIUM	Am	95	(243)
ANTIMONY	Sb	51	121.8
ARGON	Ar	18	39.9
ARSENIC	As	33	74.9
ASTATINE	At	85	(210)
BARIUM	Ba	56	137.3
BERKELIUM	Bk	97	(247)
BERYLLIUM	Be	4	9.01
BISMUTH	Bi	83	209.0
BORON	B	5	10.8
BROMINE	Br	35	79.9
CADMIUM	Cd	48	112.4
CAESIUM	Cs	55	132.9
CALCIUM	Ca	20	40.1
CALIFORNIUM	Cf	98	(251)
CARBON	C	6	12.0
CERIUM	Ce	58	140.1
CHLORINE	Cl	17	35.5
CHROMIUM	Cr	24	52.0
COBALT	Co	27	58.9
COPPER	Cu	29	63.5
CURIUM	Cm	96	(247)
DYSPROSIUM	Dy	66	162.5
EINSTEINIUM	Es	99	(252)
ERBIUM	Er	68	167.3
EUROPIUM	Eu	63	152.0
FERMIUM	Fm	100	(257)
FLUORINE	F	9	19.0
FRANCIUM	Fr	87	(223)
GADOLINIUM	Gd	64	157.3
GALLIUM	Ga	31	69.7
GERMANIUM	Ge	32	72.6
GOLD	Au	79	197.0
HAFNIUM	Hf	72	178.5
HELIUM	He	2	4.00
HOLMIUM	Ho	67	164.9
HYDROGEN	H	1	1.008
INDIUM	In	49	114.8
IODINE	I	53	126.9
IRIDIUM	Ir	77	192.2
IRON	Fe	26	55.8
KRYPTON	Kr	36	83.8
LANTHANUM	La	57	138.9
LAWRENCIUM	Lr	103	(260)
LEAD	Pb	82	207.2
LITHIUM	Li	3	6.94
LUTETIUM	Lu	71	175.0
MAGNESIUM	Mg	12	24.3
MANGANESE	Mn	25	54.9

Numbers in parentheses give the mass number of the most stable isotope.

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Element	*Symbol*	*Atomic Number*	*Atomic mass*
MENDELEVIUM	Md	101	(258)
MERCURY	Hg	80	200.6
MOLYBDENUM	Mo	42	95.9
NEODYMIUM	Nd	60	144.2
NEON	Ne	10	20.2
NEPTUNIUM	Np	93	(237)
NICKEL	Ni	28	58.7
NIOBIUM	Nb	41	92.9
NITROGEN	N	7	14.0
NOBELIUM	No	102	(259)
OSMIUM	Os	76	190.2
OXYGEN	O	8	16.0
PALLADIUM	Pb	46	106.4
PHOSPHORUS	P	15	31.0
PLATINUM	Pt	78	195.1
PLUTONIUM	Pu	94	(244)
POLONIUM	Po	84	(209)
POTASSIUM	K	19	39.1
PRASEODYMIUM	Pr	59	140.9
PROMETHIUM	Pm	61	(145)
PROTACTINIUM	Pa	91	(231)
RADIUM	Ra	88	226.0
RADON	Rn	86	(222)
RHENIUM	Re	75	186.2
RHODIUM	Rh	45	102.9
RUBIDIUM	Rb	37	85.5
RUTHENIUM	Ru	44	101.1
SAMARIUM	Sm	62	150.4
SCANDIUM	Sc	21	45.0
SELENIUM	Se	34	79.0
SILICON	Si	14	28.1
SILVER	Ag	47	107.9
SODIUM	Na	11	23.0
STRONTIUM	Sr	38	87.6
SULPHUR	S	16	32.1
TANTALUM	Ta	73	180.9
TECHNETIUM	Tc	43	(98)
TELLURIUM	Te	52	127.6
TERBIUM	Tb	65	158.9
THALLIUM	Tl	81	204.4
THORIUM	Th	90	232.0
THULIUM	Tm	69	168.9
TIN	Sn	50	118.7
TITANIUM	Ti	22	47.9
TUNGSTEN	W	74	183.8
URANIUM	U	92	238.0
VANADIUM	V	23	50.9
XENON	Xe	54	131.3
YTTERBIUM	Yb	70	173.0
YTTRIUM	Y	39	88.9
ZINC	Zn	30	65.4
ZIRCONIUM	Zr	40	91.2

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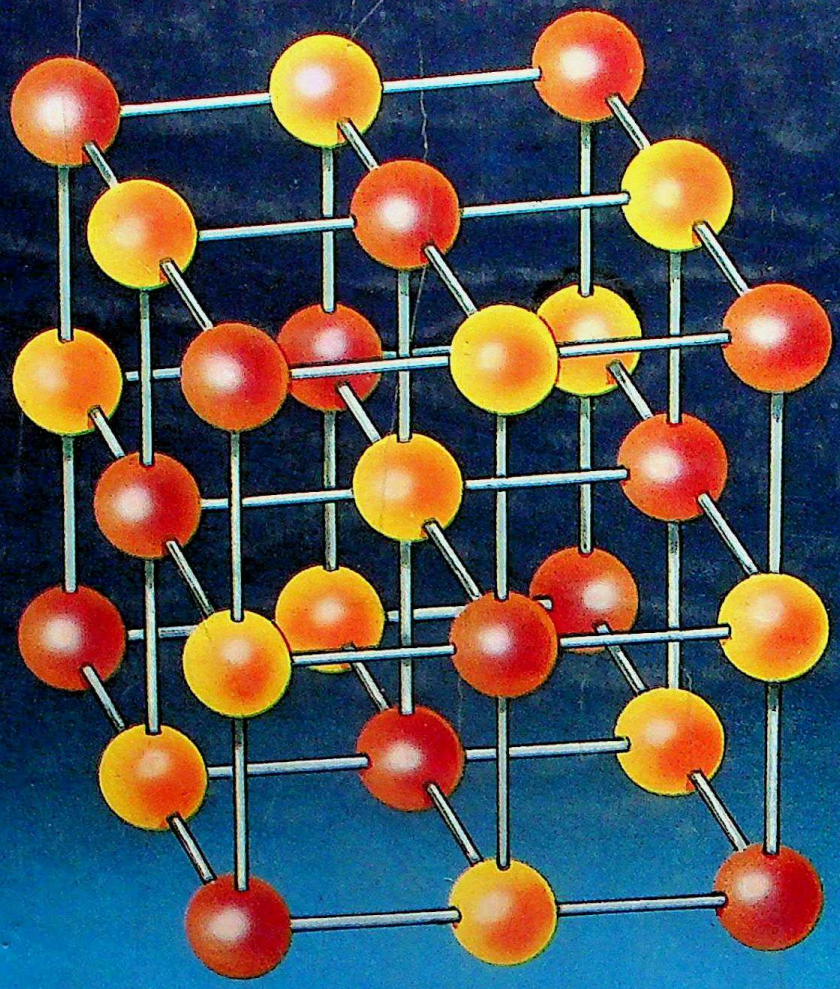

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